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EVALUATION OF MEASUREMENT METHODS AND INSTRUMENTATION FOR ODOROUS COMPOUNDS IN STATIONARY SOURCES. VOLUME II. FIELD TESTING

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Exxon Research and Engineering Company

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Three types of commercially available equipment for the analysis of H_2S and other odorous sulfides have been evaluated for performance and reliability at stack emission levels of 0.1 to 100 ppm in air. These included coulometers (3 models) flame photometric detectors plus gas chromatography (2 models) and tape sensors with or without a preliminary gas convertor (3 models). None of these instruments is capable of analyzing for H_2S in this range in the presence of large amounts of SO_2, CO_2, CO, COS and CS_2, which may characterize stack emissions from a Kraft paper mill or a petroleum refinery Claus plant. Reasons for these failures are examined, and modifications of presently available equipment are recommended for this purpose.

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Volume II, Field Testing

by

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1. INTRODUCTION

The project covered herein relates to the evaluation of instruments commercially available for the measurement of H_2S and reduced-sulfur odorants in stack emissions, under field conditions. The project started with a state-of-the-art review to determine basic requirements, covered in Volume I of this report. Instruments selected on the basis of this review were acquired on loan from the manufacturers or from EPA, and tested first in the laboratory and then in the field.

The nature of the problem changed significantly as soon as the test program began, when it became apparent that almost none of the instruments available had in fact been field tested in the stack emissions range. A single instrument, the Barton Titrator, had been used extensively in kraft mills only, and the others were either ambient instruments or prototypes. Further work was based on simple modifications of these instruments to adapt them to measurements in the stack emissions range. The following meanings are used for basic terms in this discussion.

commercial availability - an instrument which can be purchased on the open market and used for the stated purpose, as delivered. It should not require research work other than following instructions provided, either to put it on stream or to keep it in operation.

field use - the instrument can be operated with routine maintenance, in the absence of laboratory facilities (such as running water), by properly trained non-technical personnel following standard instructions. The amount of periodic replenishment needed for consumable supplies such as compressed gases or reagents should be predictable, and infrequent.

sulfur-containing odorants - the instrument should measure both H_2S and organic sulfur odorants, preferably as separate readings, free of interference from common stack gases. SO_2 can either be excluded or measured separately. Satisfactory alternates are to measure either H_2S and total reduced sulfur, or selected major individual S compounds present. These are primarily H_2S, SO_2, COS (carbonyl sulfide) and CSH (abbreviation used herein for methylmercaptan).

stack emissions - the instrument and its sampling system must be able to operate on a gas which is hot, wet, and dirty, containing percentage concentrations of water vapor, CO_2, CO and possibly SO_2, plus NO_x. The typical range of odorant emissions is about 1 to 30 ppm, or more broadly, 0.1 to several 100 ppm. Problems of interferences and sampling are very different in this range than they are in the ambient range which is more dilute, or the process gas range which is more concentrated. The ratio of potential interferants to odorants can easily be 1000:1, or more.

None of the instruments available proved capable of making the routine measurements desired, in the refinery and paper mill stacks selected for field testing. Accordingly, the procedure for their quantitative evaluation was modified (1) to achieve operability, then (2) to develop their relative advantages, disadvantages and problems encountered. The selection of procedures and instruments will first be considered in more detail.

Acknowledgment is made of the effective assistance of Mr. Leigh Gove as research technician throughout this project, and Messrs. G. J. Piegari and A. C. Hall as engineers, F. W. Church and R. S. Brief as staff advisors, and P. K. Starnes and P. B. Gerhardt as analytical consultants. Invaluable cooperation and hospitality were received from the Exxon Company, U.S.A. (former Humble Oil and Refining Company) in providing a site for refinery field tests, and from the S. D. Warren Mill of the Scott Paper Company at Westbrook, Maine for paper mill field tests under the direction of Messrs. R. P. Labrecque and S. T. Broaddus.

Loans of equipment were arranged through the courtesy of Messrs. Robert K. Stevens and Fredric C. Jaye of the Environmental Protection Agency, John Robison of ITT Barton, Oliver Cano of Bendix Process Instruments, Charles Kimbell of Houston Atlas, John Rex of Research Appliances Corp., Frank Kabot of Philips Electronic Instruments, R. J. Joyce of Dohrmann Envirotech, and Troy Todd of Tracor, Inc.

2. SELECTED APPROACH

2.1 Selection of Instruments

Three principles of measurement were selected for study: coulometry, flame photometry, and lead acetate tape sensing. Eight instruments using these principles were acquired on loan, or on nominal rental. These are listed in Table 1, and manufacturer's claims for these instruments are summarized in Table 2. Four varieties of coulometers were included, two flame photometric detector systems (FPD) combined with gas chromatography (GC), and two lead acetate tape sensors ($PbAc_2$):

Table 1

Principle and Instruments	Auxiliary Equipment
Coulometry	
Barton Titrator	SO_2 bubbler, chemical absorption system
Dohrmann Microcoulometer	
Oxidative Cell	Pyrolysis furnace, independent GC
Reductive Cell	Direct injection or sample valve
Philips SO_2 Monitor	Dry absorption filters (ambient)
GC + FPD	
Bendix	None; integral unit
Tracor	Separate "function selector"
PbAc2 Tape Sensors	
Houston Atlas	Pre-pyrolysis + catalytic reduction
RAC	Dynamic dilution

TABLE 2

MANUFACTURERS CLAIMS (INSTRUMENTS AS OF 1971)

Instrument + Method	Ranges: ppm H_2S	Measures			Time Cycle	Zero drift, 24 hrs.	Accuracy ± % FS	Repeatability	Unattended Operation
		Total S	Compounds	COS					
	(7)								
Barton 400 Br/HBr Cell	.010-1000	Yes	all together	No	Continuous (1 hr. for timed filter system)	reset	4% at 10 ppm	4%	7 days
Bendix 8700 GC/FPD	(11)	Yes	TS/H_2S/SO_2	as H_2S	5 min.	1% (2% 3 days)	2%	1%	7 days
Houston-Atlas	(3)								
825 $PbAc_2$ Tape	.010- 20	No	H_2S (low SO_2) (Ag tape, ± SO_2)	No	Continuous	(2%)	--	5%	Yes
855 + red. to H_2S	Same	Yes	all together	Yes	Continuous	1%	--	5% (linearity)	Yes
RAC 5000 $PbAc_2$ tape	.001 to .15	No	H_2S (low SO_2)	No	5 min. multiples	(2%)	15-30%		Yes
Dohrmann									
oxidative MC 301 furnace, I_2 Cell	.1 at 10 µl to	Yes	GC effluent	Yes	pulsed injection	reset	10%	5% (at 10 ppm)	No
reductive MC 401 Ag Cell	200 at 2 µl	No	H_2S, CSH direct	Yes	pulsed or continuous	reset	5%	8% (at 10 ppm)	No
Philips PW 9700 Br/KBr Cell	.010 to 5	No	H_2S or SO_2	No	Continuous	.01 ppm	.01 ppm	2%	90 days

The principles of operation of these instruments and the basis of their selection are discussed more fully in Volume I of this report with literature references which should be consulted for further information. Auxiliary equipment required for each instrument is listed separtely, because it had an important bearing on the performance of the instrument in every case. The failure or inadequacy of this equipment for field use ruled out at an early stage the Philips, Dohrmann oxidative system and Tracor instruments as originally acquired, leaving five instruments for the bulk of the program. These were primarily the Barton, Bendix, Houston Atlas (combination unit) and RAC, plus the Dohrmann reductive cell.

2.1.1 Instruments not Tested

The Philips SO_2 Monitor enjoys an excellent reputation for good engineering and reliable field performance in the measurement of ambient concentrations. Its instruction manual is the best and easiest to use of all the instruments received, and the laboratory data obtained were in line with manufacturer's claims. It was dropped before field evaluation for four main reasons:

(a) The maximum range to which it could be adjusted by the manufacturer for direct measurement of H_2S was below 5 ppm. This is barely above the ambient range, and too low to be useful for monitoring even a well-controlled stack without dilution.

(b) The barium acetate filter system provided to remove SO_2 when measuring H_2S is designed only for ambient use. It is rapidly exhausted when the sample contains a large excess of SO_2, which is characteristic of many stack emissions. Also, no provision is available for switching filters so that the same unit can be used for either H_2S or SO_2.

(c) Safety features built into the instrument limit its use to ambient pressure. It could not accept even a 1 mm (Hg) temporary pressure fluctuation, on starting gas flow from the manifold used to distribute gases to the instruments on test. This could probably have been corrected.

(d) Very poor service was received from the manufacturer in attempts to adjust the filter system and the instrument's safety pressure controls for our use. Service was good on routine maintenance, but anything not routine was referred to the home office in Holland, which took six months or longer for a reply.

The Dohrmann Microcoulometer has many operating requirements which are difficult to achieve in the field. First is the necessity for daily calibration, changing the cell electrolyte, and constant skilled attention to keep the instrument in adjustment. The oxidative cell system converts all sulfur compounds present to SO_2 using a high-temperature pyrolysis furnace, which has a large demand for cooling water. A portable system for cooling water was tried out but this proved to be an undesirable nuisance, and tests on the oxidative cell were discontinued. A limited amount of further testing was carried out on the Dohrmann reductive silver cell, which has the advantage that it responds to either H_2S or mercaptan but is not sensitive to SO_2. This unit could be operated in the field, and gave somewhat smoother results in continuous operation than on spot samples. This was of strictly limited interest, however, because the electrode was consumed as well as the electrolyte.

A Tracor Model 250H unit combining GC/FPD was loaned to the project by EPA, as a possible alternate to the Bendix unit using the same approach. The Tracor system was essentially a prototype with separate boxes housing a "function selector" for electronic controls, and the equipment for separating and sensing. The function selector box was inoperable as received, due to damage in shipment. Reasons for this could not be diagnosed with the incomplete operating manual supplied, and the control box was returned to the manufacturer at his request. It was apparent that the GC oven and other parts of this equipment were not as far along in engineering as the Bendix unit, and no further tests on it were made. An improved Model 270H has been announced during 1972, combining the function selector and other equipment in a single box.

2.1.2 Initial Adjustments to Test Instruments

The Barton Titrator was ready to go on stream as received. Two modifications were made after initial laboratory tests. A one-liter surge pot was removed from the sample line, to give a much more rapid instrument response. This surge pot has several functions which are discussed further below, one of which is to decrease the sensitivity of the instrument to short term variations in sample composition. With this more rapid response, the recorder chart speed was set at 30" per hour instead of the analysis. It is present in many refinery emissions, particularly those produced under reducing conditions. In some cases, such as the stack gas from a Claus plant after-burner, it may be found in much larger amounts than the residual concentrations of H_2S. COS can also occur in the stack gases from a kraft mill recovery furnace, particularly under overload conditions. Unfortunately, it creates severe analytical problems with the potassium acid phthalate scrubber system used by Barton to separate SO_2, if the sample is a COS-containing gas. This had not previously been described. CS_2 in large amounts is also an interferent in the Barton.

Heavier sulfur compounds in the kraft mill effluents are chiefly dimethyl sulfide (CSC) which is the thio-ether of methyl mercaptan, and dimethyl disulfide (CSSC), an oxidation product. These compounds may occur in relatively high concentrations in process gas streams within the pulping process, but their amount in kraft mill effluents is normally less than the CSH from which they are derived and much less than the amount of H_2S. They can appear, however, and make a significant contribution to total odor effects, whenever emissions are uncontrolled or temporarily out of control. A somewhat analogous situation applies to the varying amounts of carbon disulfide which may be emitted from a Claus plant burner stack. The total amount of CSH, CSC, CSSC and heavier sulfides present is included in any measurement of TRS, or the difference between TRS and H_2S. The control procedure usually preferred is to collect all emissions containing collectible amounts of any of these odorants, and incinerate to SO_2.

2.2.2 Laboratory Gas Samples

The gases primarily considered in this study were H_2S, SO_2, COS, and CSH. Working gas samples of each of these were prepared as blends in nitrogen, as listed in Table 3, and stored as compressed gases in No. 1A cylinders. These cylinders were each aged with the gas blend before filling and initial analysis by the manufacturer. This gave good results except for H_2S. No satisfactory method of preventing the decay of H_2S in steel cylinders was available, and an aluminum cylinder was no better. A Teflon-lined cylinder gave even poorer results, since the concentration of H_2S which it delivered went down and up inversely to the temperature to which the cylinder was being exposed. In steel cylinders the decay rate tended to fall off with time, so the gas could ultimately be used at a known lower concentration.

Table 3

Working Gas Blends

Sample Gas	Blend in N_2		Changes in Use
H_2S	Nominal	125 ppm	(Decayed gradually to 24 ppm)
		200 ppm	(Used mostly at 180 ppm)
		74 ppm	(Used mostly at 30 ppm)
		51 ppm	(Teflon-lined, mostly 70-85 ppm)
SO_2	Nominal	670 ppm	
		22,700 ppm	
COS/CS_2	Nominal	2460/255 ppm	
		Diluted to 246/26 ppm	
H_2S/CSH	Nominal	205/195 ppm	
CSH/CSC/CSSC	Nominal	505/510/490	
		Diluted to 50/51/49	

Concentrations of H_2S in these working blends were calibrated against permeation tubes in a constant temperature bath, as recommended by Stevens (1) and O'Keefe(2).

2.3 Test Sample Requirements

2.3.1 Gas Manifold

Initial laboratory tests indicated that all the instruments respond at once and in direct proportion to any change in inlet pressure. Special provisions are required whenever two or more instruments are connected to the same manifold, to avoid a disturbance to all the instruments when any one of them passes through a cycle which involves a change in flow. Tests in parallel also require that the pressure within the sensing cell of all instruments be the same. This is complicated by the fact that each instrument as received has its own pump or aspirator system, with a different capacity or gas flow rate. The expedient of using an oversized gas manifold to minimize these effects was ruled out for this program, because it involves time delays and gas mixing which is undesirable with samples of continually changing composition.

The effect of sample gas pressure on instrument reading is a simple matter of physics. It is recognized in the manuals, but still frequently overlooked. The effect of barometric pressure within the sensor, for example, is almost never controlled, and yet it alone can cause variations of 5% in readings on the same sample. While the effect of ambient temperature may be greater, as much as 10% or more, it is frequently controlled. A more frequent source of error is to depend on a gas rotameter to measure flow rates. These instruments repond to changes both in gas pressure and composition, and it is only when these variables are held exactly constant that the necessary corrections for them can be ignored.

---

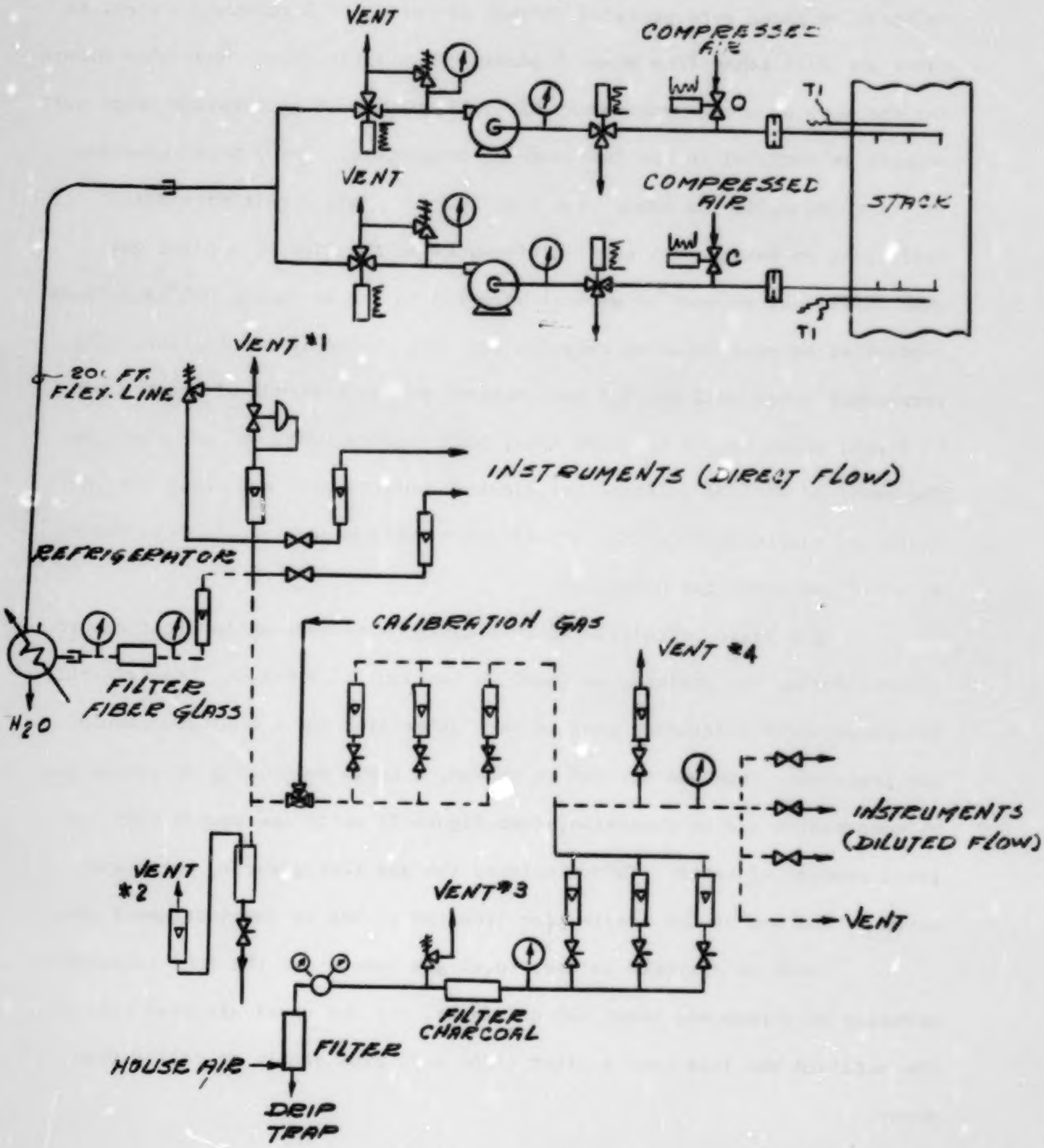
(1) See Bibliography.

A pressure controlled manifold system was constructed to minimize these problems, and used both in the laboratory and in the field. It was operated at a positive pressure of 2 psig at all times. This was accomplished by feeding into the manifold an amount of gas equal to 30% or more above the total demand of all instruments on line, and bleeding the excess gas to vent through a simply but accurate Moore pressure release valve (63 SDL). The manifold pressure was let down into the inlet of each instrument through a solid block needle valve, and monitored by an open-end mercury manometer which was held at a constant level against the instrument pump or other feeding system.

The design basis of this manifold is shown in Figure 1. This was designed to be compatible with a sampling system for field use to provide a constant supply of sample at all times during any purging or cleaning cycle, starting with dual stack probes and sintered porous metal filters. Compressed and de-watered sample gas was passed through a heated 3/8" Teflon line (up to 200 feet used). The same gas manifold was used both in the laboratory and in the field. Excess gas was vented to the atmosphere after every gas measurement point, for dynamic balance. Bleed lines just past the inlet points for dilution air or calibration gases were used for more accurate control of gas flows, rather than for the control of pressure. The principal pressure release point through the Moore valve was placed at the end of the manifold, past all the instrument feed lines, to minimize the effect of valving changes in any one instrument on gas flow to the others.

Figure 1

DESIGN OF PROBES AND GAS MANIFOLD


VENT
COMPRESSED AIR
T1
O
VENT
COMPRESSED AIR
STACK
C
T1
VENT #1
20' FT. FLEX. LINE
INSTRUMENTS (DIRECT FLOW)
REFRIGERATOR
CALIBRATION GAS
VENT #4
FILTER FIBER GLASS
H_2O
INSTRUMENTS (DILUTED FLOW)
VENT #2
VENT #3
VENT
FILTER CHARCOAL
HOUSE AIR
FILTER
DRIP TRAP

Flow controls for either dilution air or large volumes of calibration gases were provided through batteries of 3 rotameters each, to cover the full range from about 5 cc/min. to 3 liters/min. Mass flow meters for the more accurate measurement of small volumes of calibration gases were mounted in parallel to the last bank of rotameters. These were sensitive to ± 1 cc/min., in the range from 1 to 100 cc. This sensitivity was sufficient to detect very small differences in the flow of a given gas when additional amounts of another were fed to the manifold; all rates were controlled or readjusted as required for each change in composition. The permeation tubes used for H_2S calibrations produced blends of about 3 ppm to 9 ppm, depending on the tube size, bath temperatures, and air flows to the manifold of 1 to 2 liters per minute. Outlets were available for the supply of sample gas directly to different instruments in parallel, before or after the final gas dilution.

The basic principles of this design were kept while details were altered during the project, as shown in Section 2.3.2 below. The original design provided a separate pump in each probe line for a positive sample gas pressure. This was altered to provide a rapid dewatering of sample gas by compression and re-expansion, (see Figure 2) using the second pump for rapid removal of water. This displaced the gas refrigerator, which was moved to the end of the sample line from the probes to the instrument van.

With this system in use, total gas demand for the four instruments normally on stream was about 600 cc/minute, and the usual air feed rate to the manifold was just over a liter (1060 cc), plus sample or calibration gases.

2.3.2 Field Sampling

The problems of getting a satisfactory gas sample for analysis from a stack gas which is hot, wet and dirty are well known and chronic. This is particularly true of efforts to get a continuous sample gas flow, which have usually been abandoned in favor of taking a spot grab sample. The situation is worse for odorants which must be measured at low ppm or ppb levels than it is for the usual combustion gas components, which occur at higher concentrations. The problem is partly mechanical, partly physical, and partly chemical. Excess water vapor drops out as soon as the hot gas is cooled below its dew point, which is of the order of 140-180°F. This water appears in the lines as a mixture of slugs in gas. This is difficult to pump, and the whole length of the line can act as a gas scrubber or chemical reaction zone. The degree to which this changes the composition of the final gas is variable, depending on time and temperature and the possibility of interactions between the gas and any particulates present. All such changes are undesirable, and they can easily destroy the integrity of the sample.

These problems are aggravated if the gas is to be pumped through the sample line at any pressure above atmospheric. This increases the solubility or reaction rate of gases, raises the dew point, and thus makes it more difficult to prevent condensation by using heated lines. Once condensate has been formed in a line, the amount of heat which can be supplied through ordinary heating is not enough to cause much re-evaporation.

A common expedient to reduce this tendency to condensation is to run the sample line under reduced pressure, using a pump or aspirator. The problem is that air leaks into the system are difficult to avoid, easy to ignore, and hard to detect. "Quantitative" results reported with a leaky sample line under these conditions may be analytically correct but always too low, by an unknown amount. The alternate expedient of diluting the stack gas promptly with air to below its dew point involves large uncertainties in temperature/volume corrections, and is less desirable than direct measurements.

A solution to these problems requires a method of rapidly removing both particulates and excess water with a minimum of contact between sample gas and any condensate, and keeping the sample above its dew point for the largest possible fraction of the total time until it reaches the analytical sensor.

A field sampling system was designed and built to supply sample gas under pressure, without hot dilution, with low hold-up, and with minimum scrubbing effect from any condensate. It consists of five elements:

(a) Two probes in parallel, alternately on stream at all times while the other is blown back with air, each probe including an integral filter inside the stack.

(b) A combination of three knock-out traps and two pumps in series placed next to the stack, which dewaters the sample gas rapidly at ambient temperature and 10-20 psig, and feeds it to the sample line.

(c) A heated line which keeps the sample gas above its dew point until it reaches the instruments.

(d) A gas refrigeration unit with a centrifugal separator which chills the sample rapidly to about 40°F at the instrument end of the line, and removes any residual condensate without further contact with the sample.

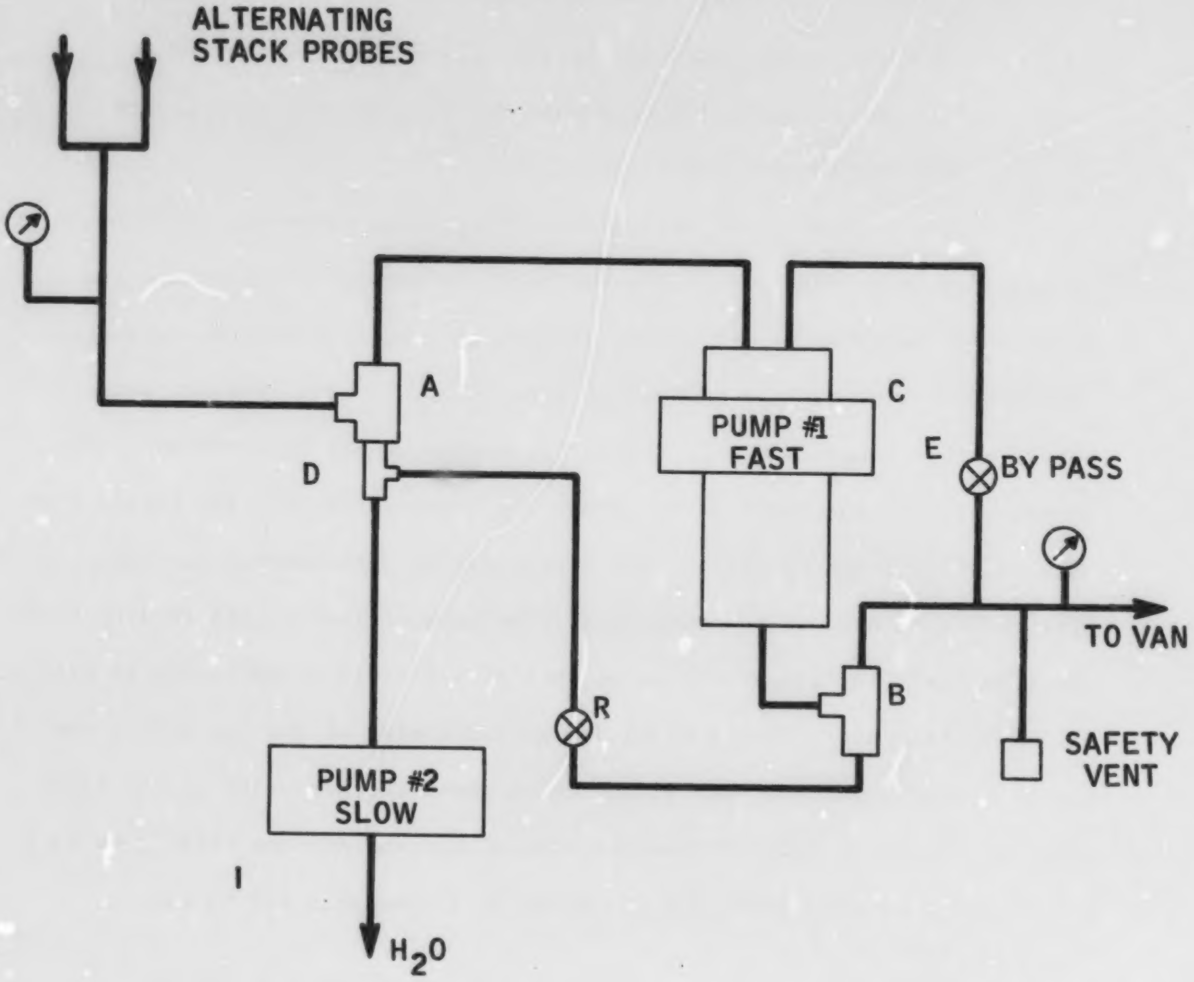
(e) A pressure-reducing valve on sample fed into the instrument manifold, either directly or plus diluent air if desired. Both the pressure reduction and any dilution gas help to prevent any further condensation.

The system of two probes with alternating blow-back is shown in its initial design in Figure 1. This was built to provide a continuous gas flow, from one probe or the other, without interruption for the necessary intermittent blow-back by a blast of air. Air blow-back operates satisfactorily with a single probe in the Barton system, where it produces a blip of air which is entrapped in the probe and transferred into the sample line once in every 5-minute cycle. The single system with intermittent air flow cannot be used in the testing of a battery of instruments feeding from the same manifold, since varying amounts of air could be delivered to different instruments. In the final design the timing of the two probes was set by a repetitive self-energizing cycle, where the air blast in the first started 30 seconds after the second came on stream, and the first came back on stream 30 seconds after the air blast to it was shut off by the timer.

The pump-trap combination detailed in Figure 2 was primarily responsible for the success of this system. It was added to the sampler after the initial combination of dual probes, pumps, heated lines and

Figure 2

PUMP-TRAP SYSTEM FOR RAPID WATER REMOVAL


ALTERNATING
STACK PROBES
A
C
PUMP #1
FAST
E
BY PASS
D
TO VAN
R
B
SAFETY
VENT
PUMP #2
SLOW
I
H_2O

refrigerator as shown in Figure 1 failed repeatedly in the same service. The failures were caused partly by the uneven swelling of gas-resistant flapper valves in the diaphragm pump, which could handle either water or gas but was not able to handle alternate slugs of water and gas. The successful combination adds a double gas recycle and low-volume water traps (A, B, D). The primary gas recycle returns compressed gas from the second knock-out trap (B), after the compressor (C), at a variable ratio from 1/1 to 10/1. The water from this trap (B) passes through valve (R), to the third trap (D) to disengage and return entrained gas, along with the fresh feed. This minimizes sample demand through the probes. The compressed gas which is recycled through valve (E) has been dewatered by compression, while feeding a limited amount of fresh sample to the primary trap (A). This decreases the excess water load on the compressor (C). The rate of water removal pumped (I) from the third trap is adjusted to vent a minimum amount of gas, usually about 500 cc/minute, with a fresh sample feed of 2 to 4 liters/minute. A minimum amount of fresh feed is desirable to limit the amount of heat dissipation required in the line from the probes to the Teflon air-blow-back valves, nearest the stack.

Teflon lines were used throughout, and the use of Teflon valves in the hot gas line at the stack was felt to be particularly important to minimize sample degradation. These valves were part of the standard control system provided with the Barton probe. Existing equipment was used here to simplify the design. The pump diaphragm was Viton, which is said by the manufacturer to show less tendency to swell than other elastomers in SO_2-containing gases. The probes, traps (pipe-T's), pump body and refrigerator were made of 316 stainless steel. This use of metal parts would not be permissible in a system designed for the ambient gas range, below 1 ppm. Laboratory tests at an early stage of the program showed that stainless steel fittings cause a loss in H_2S in air of a fraction of one part per million, on contact with the metal. This can be severely limiting in analyses at the 1 ppm level, and catastrophic below it. The same loss has much less effect at ppm levels, and progressively less at normal stack concentrations. Any effect that it has in this range is comparable on all samples tested at the same time, and can therefore be ignored for purposes of comparison.

The water removed from the refrigerator trap was normally odorless and showed no evidence of elemental sulfur. Water removed from the initial knock-out traps was also nearly odorless, and showed barely detectable amounts of 4 to 16 microliters of H_2S and SO_2 per liter on colorimetric analysis.

2.3.3 Effects of Water Vapor on Specific Instruments

The amount of water vapor in the system is an important difference between laboratory and field conditions. Excess water has a specific effect on many instruments. Tape samplers are designed for a gas which is moist, but not wet. A certain amount of moisture is necessary for the $PbAc_2$ tape reaction, but too much can wet the tape and cause it to break. Both tape samplers tested had a humidifier vessel, designed to trap excess water or supply it if the gas was too dry. This system was a source of trouble with both instruments. The RAC had a simple water bottle in which the gas impinged on the surface. The RAC could not be used in a plant environment with ambient air or unanalyzed plant air as a diluent, containing uncontrolled trace amounts of S, and the use of dry compressed air caused the humidifier bottle to evaporate in a little over a day. The Houston Atlas humidifier uses a 5% aqueous acetic acid trap to either add or remove water, and this does not disappear as fast with normal gas flow. The system gave problems with the carryover of spray from the humidifier into the sensing head, where it wet the tape and caused intermittent breakage. Partial condensation or back-pressure in the elevated vent line may have been a factor. The 1972 model of this instrument has been able to eliminate the bubbler for samples in air, by balancing the amount of water vapor formed in the catalytic reduction against that required for the tape.

Stack gas samples are very wet. The amount of water vapor commonly present in a kraft mill recovery furnace stack is 20 to 40%, and a 30% volume shrinkage is assumed in the usual routine calculation of the concentration of sulfur compounds in the gas as emitted, based on gas as analyzed. Similar moisture contents appear in the stack gas from a Claus sulfur plant, which produces one mole of water for every mole of sulfur.

In addition to mechanical problems in sampling, this excess moisture limits the choice of GC packings which can be used for any gas separation desired. It is not a problem with the polyphenyl ether packing used in the Bendix as supplied, or with Poropak Q. It is measured by Poropak R, which is a limitation if H_2O is present in very large amounts. It destroys the activity of silica-base materials such as Deactigel, which is one of the packings recommended for separation of COS from H_2S. These effects may be moderated or controlled by the use of a guard bed and backflushing, but it is simpler if possible to select a packing which is not so affected.

Sulfur dioxide has more of a tendency to hold up in sample lines in the field than in the laboratory. This reflects the influence of moisture which tends to plate out in the lines with the SO_2, as sulfurous acid. Line adsorption of moist SO_2 can be critical, and significant even in Teflon lines at highly variable concentrations.

2.4 Data Logging

2.4.1 Instrument Output Limits

The output signal from each of the five instruments on test was designed or adjusted by the manufacturer to 0 - 100 millivolts, full scale. The Barton, Houston Atlas and Dohrmann give a continuous measurement, and each has its own strip chart recorder. The Bendix gives a separate output for each of three GC peak heights, on demand or on a 5-minute timed cycle, and does not need a recorder for routine operation. A continuous output to record the GC/FPD signal is available, if desired. This is useful for the study of column behavior or the analysis of unknown samples. The output from the RAC is a continuous timed reading of cumulative spot density, fed normally to a meter. Its cycle can be set on any multiple of 5 minutes up to 4 hours.

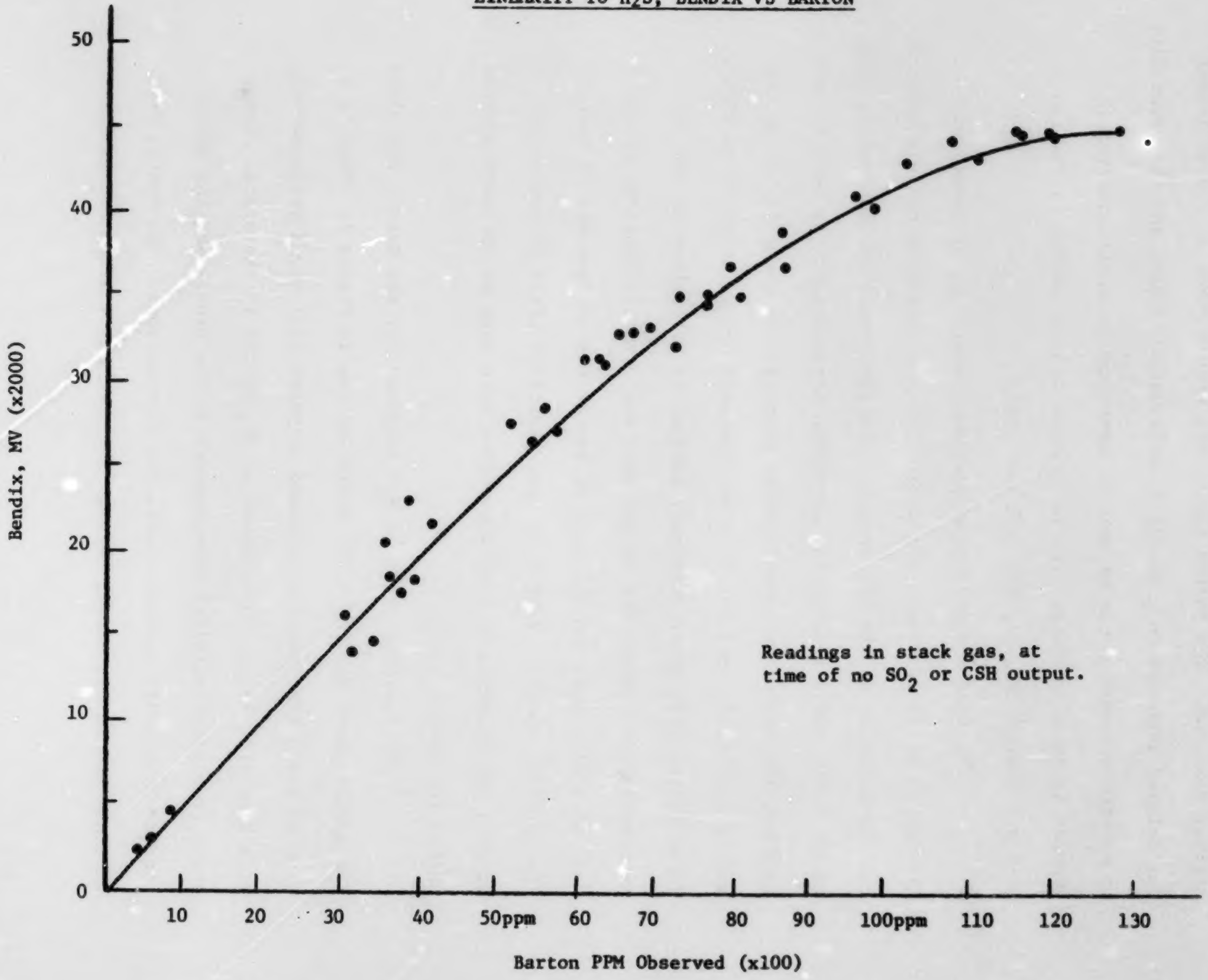
The Barton sensor gives a useful output well beyond the upper limit of its recorder scale. Its ability to give approximately linear results up to 300% of scale is a practical advantage. This may be used to avoid the complete loss of data under conditions of unexpected overload, if it is linked to an auxiliary system such as a meter or a digital read-out. The Barton electronic system gives an almost linear but delayed response to a change in attenuation scale, and the capability to operate over-scale can be used to advantage to avoid undesirable changes in scale setting. The instrument is most useful in the top 5 of its 7 scales, x1, x3, x10, x30 and x100.

The Bendix system responds immediately and arithmetically to changes in scale setting. Its upper limiting factor is not electronics, but the capacity of the FPD sensor. The instrument has 11 scales, from x1 to x2000, and a setting for automatic attenuation. As used in this program, the signal was consistently overscale at about 115 MV on the x50 or x100 scale used for most measurements, or at about 45 on x2000. These limits were quite constant, subject to variations in the corresponding zero base. The Bendix zero was normally constant within 0.5% of scale, and much the best of any of the instruments on test. The specific model on test lost zero stability after 10 months on stream; improvements to this sub-system were made by the manufacturer during the year.

The limiting value of H_2S response for the Bendix was about 120 ppm,as shown for the x2000 scale setting in Figure 3. This is a plot of field test results obtained in paper mill stack measurements, at a time when Bendix data showed no SO_2 or CSH in the stack. Under these conditions parallel measurements in the Bendix and the Barton provide a reliable extended basis for correlations. The Bendix MV readings are fairly linear through 100 ppm, but flatten out rapidly

FIGURE 3

LINEARITY TO H_2S, BENDIX VS BARTON



Readings in stack gas, at time of no SO_2 or CSH output.

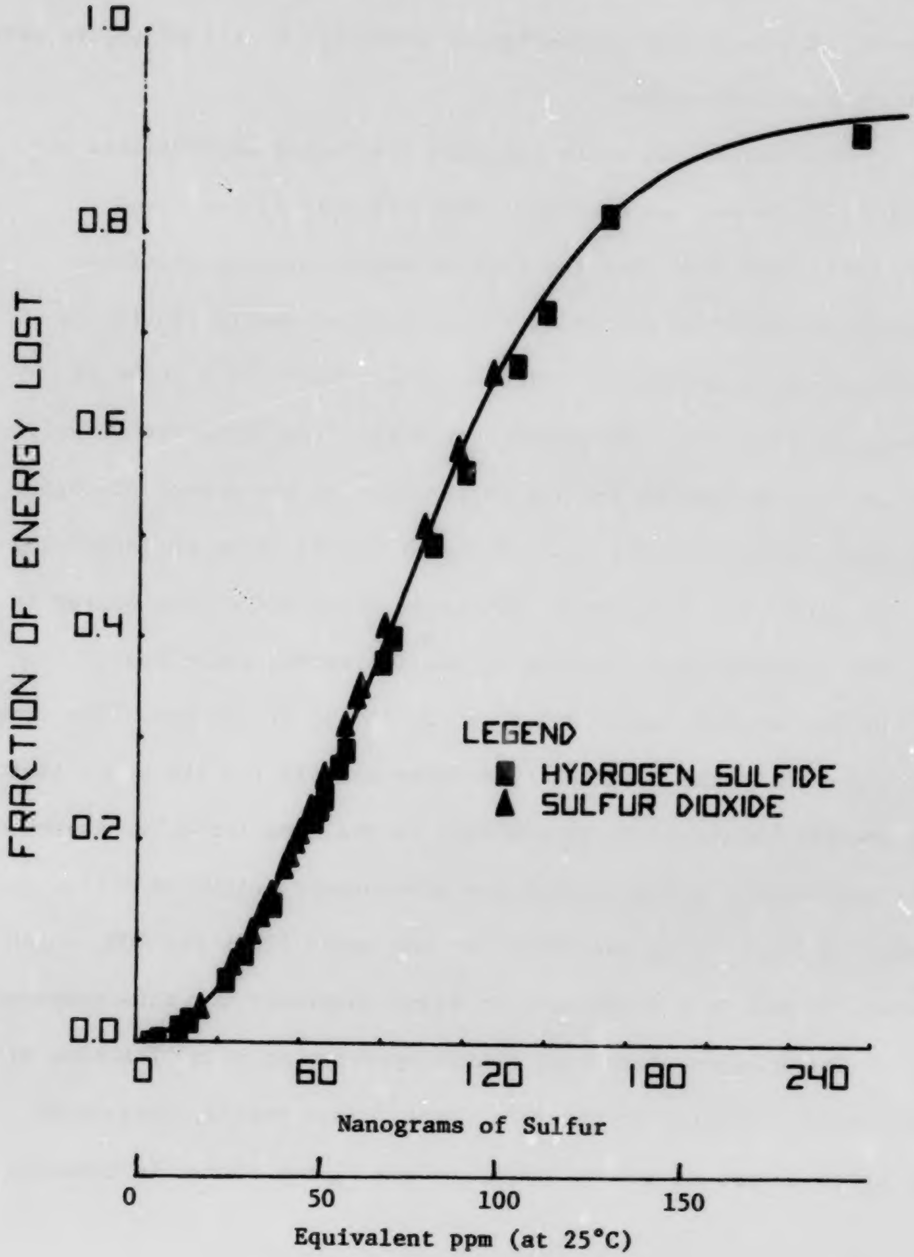
above this. All concentrations above 120 ppm are off scale and give the same reading of 45-46 MV. Other data show that the off-scale level at x1000 is 88-89 MV, or almost exactly linear (two times 45). The limit is correspondingly higher at lower attentuations, but with less difference between scales, appearing at about 113 to 115 MV (above zero) for the x100 and x50 scales.

The theoretical basis for this flattening which places an upper limit on output has been developed recently by Greer and Bydalek (3). They find that the loss of sensitivity of the flame photometric detector at higher sulfur concentrations is due to the self-absorption of the energy emitted. Their basic data curve is reproduced in Figure 4. The conversion scale from nanograms of sulfur (by weight) to ppm is 75% for a 1 cc sample. As the amount of sulfur in the flame increases, the loss of energy increases at an increasing rate. The inflexion point is at 100 ng,at which 50% of the energy is lost. This corresponds to 75 ppm in the instrument under test. The curve flattens sharply above 80% loss, at 160 ng or 120 ppm. The experimental curve in Figure 3 checks this value exactly for its upper limit. The volumetric relationship in ppm will be the same for other gases, such as SO_2 or CSH, which contain one gram atomic weight of sulfur per mole. A lower value was found for the upper limit for COS, which may be attributed to a difference in flame chemistry for this compound.

The Houston Atlas tape sensor operates at a low fraction of the saturation capacity of the $PbAc_2$ tape. As a result, instrument output up to 25 ppm is nearly linear on scale, but overscale capacity

FIGURE 4

ENERGY LOSS IN FLAME PHOTOMETRIC DETECTOR[3]



is limited. Sample dilutions for scale changes are made by a variable sector on a 20 second timer. This controls the percent of sample flow which passes into the conversion chambers, or is vented. The reproducibility of the timer setting is about ± 1% on full scale. This becomes ± 10% of reading at a dilution of 10:1, however, and correspondingly more at higher dilutions. The small rotameter and valve supplied with the instrument are not sensitive enough to cut back on sample flow per unit time for higher concentrations, and a more accurate control system was added for some tests. Zero adjustment is set manually as desired for the reflectance of each tape. This is subject to normal variations of ± 2-3% FS at zero for a given tape, at all levels of reading, with occasional spikes of -10% at a constant gas input.

The logarithmic output and narrow range of the RAC instrument is a serious limitation, except at a very low concentration. The undiluted range of the sensor is 0.001 to 0.100 ppm. This is multiplied by dilution, but only the lower half of the scale is approximately linear. The output in terms of percent transmission was converted to percent absorption for convenience in recording, by subtraction from a constant bucking voltage. If logarithmic data are to be used in the unconverted form, the exact time of starting the absorption cycle is critical and not well-suited to data logging. A computer calculation to eliminate this need is possible, but it requires recording enough data points to determine differences in slope. This means taking one minute readings, which is a nuisance for the other instruments, if the RAC cycle modulus is cut to the minimum of 5 minutes which was necessary for samples of a concentration higher than 10 ppm. This calculation if made, however, eliminates the necessity of determining or assuming an accurate zero for the tape spot in each cycle. Similar advantages could be realized by providing a linearizing circuit to convert the logarithmic output to a direct measurement of slopes.

The Dohrmann cell can operate as a continuous sensor for TRS within the limit of its capacity, or for the measurement of discrete injected samples. The instrument can be used on stream or tied to a GC or other pretreatment system. The normal output is the area under a GC peak, which is calculated by a disc integrator but read manually to interpret the results. The problems inherent in the Dohrmann system do not encourage repetitive sampling of a variable stream. It is necessary to make critical adjustments of electronic bias, gain, and range to get a well-shaped curve which starts and ends at zero. These adjustments establish a base line which may vary with each sample, and without them, the results are difficult to interpret. When the cell is used as a continuous indicator for TRS, these adjustments are not so critical. The output is proportional to total concentration of H_2S, CSH, and COS in part (10-15% response), but not SO_2. This is a useful combination for total sulfur, but its capacity in this service is strictly limited by the consumption of the electrode as well as the electrolyte.

2.4.2 Recording System

A data acquistion system was designed and built to accept the simultaneous input of all instruments, print out their MV readings in parallel for comparison, and store the data for the calculation of standard deviations. These calculations are based on entries selected by manual inspection of the printout. The recording system comprised three basic elements:

a) An Esterline Angus D-2020 Data Logger

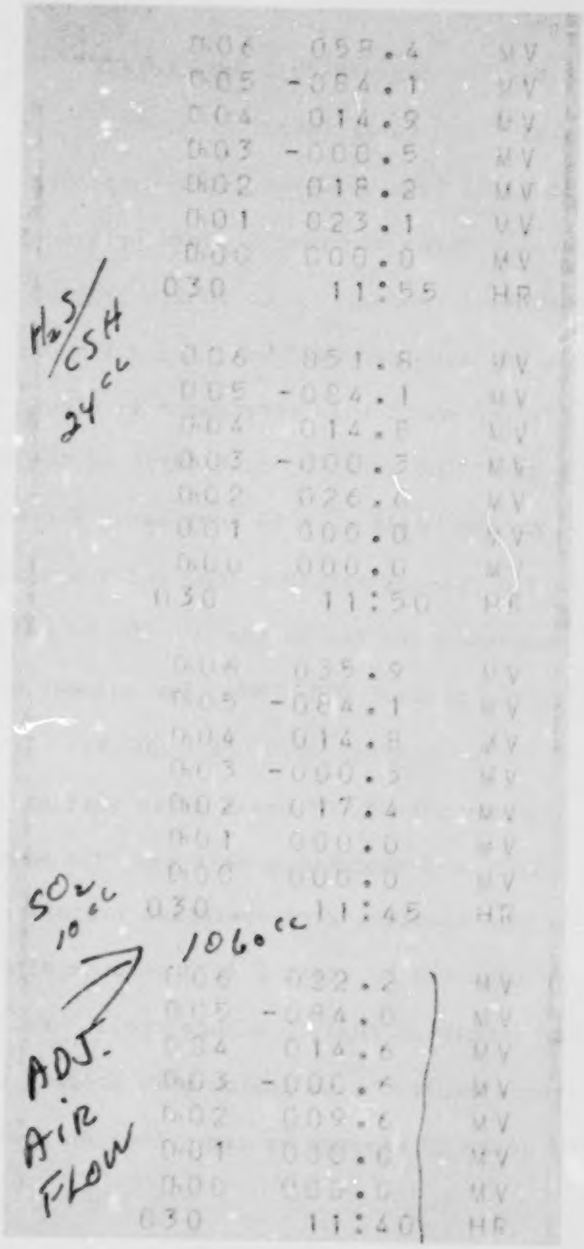
b) A Tally P-120 Paper Punch

c) An IBM 1130 Tape Reader-Printer-Computer.

The Esterline Angus provides its own printed tape output. Readings on any number of channels up to 20 are printed in sequence in a single column, and simultaneously digitized for external output. A typical set of printed entries is reproduced in Figure 5. The first line in each entry gives the date (by last digit of the month, and day) and the hour (HR), on the basis of a 24 hour day. Succeeding lines give the number of the channel recorded (Ch) and its reading in millivolts (MV). The instrument as set on the 0 - 100 MV scale records the outputs received to the nearest 000.1 MV. Any channel can also be set if desired to read to the nearest 00.01 or 0.001 MV. It can read and print about one line per second, or about seven entries per minute when reading seven channels on a continuous setting. The normal setting was to read once every five minutes, when operating properly. The time cycle of this setting was adjusted to start 2 to 5 seconds after the Bendix and RAC instruments had completed their 5 minute cycle. Readings every minute were taken when it was desirable to follow more closely the output of the Barton or RAC, and every 20 minutes or every hour on most overnight runs.

FIGURE 5

ESTERLINE ANGUS TAPE RECORD



```
006   058.4   MV
005  -084.1   MV
004   014.9   MV
003  -000.5   MV
002   018.2   MV
001   023.1   MV
000   000.0   MV
030     11:55  HR

006   051.8   MV
005  -084.1   MV
004   014.8   MV
003  -000.5   MV
002   026.6   MV
001   000.0   MV
000   000.0   MV
030     11:50  HR

006   035.9   MV
005  -084.1   MV
004   014.8   MV
003  -000.5   MV
002   017.4   MV
001   000.0   MV
000   000.0   MV
030     11:45  HR

006   022.2   MV
005  -084.0   MV
004   014.6   MV
003  -000.6   MV
002   009.6   MV
001   000.0   MV
000   000.0   MV
030     11:40  HR
```

H_2S/CSH 24cc

SO_2 10cc

1060cc

ADJ. AIR FLOW

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Except for persistent and annoying mechanical failures in the Esterline Angus unit, this system worked well as designed. No problems whatever were encountered with the Tally Paper Punch.

The IBM 1130 was programmed to read the paper tape and feed it into disc storage. Each tape normally represented one day's operation, or a longer period such as a week-end with less frequent entries. Four computer programs were set up for this project (see Appendix I). Program 1 reads the tape and stores up to 300 entries, for any number of channels up to 12 per entry. The number of channels entered is kept to a minimum, depending on the number of instruments on stream. This allows more frequent entries if desired. For extra long tapes the tape reader stops after the first 300 entries and waits for printing and processing the first 300 before it is started again to continue reading. The disc was used for temporary data storage of the daily record and discharged each time another set of entries was read.

Program 1A reads the disc and prints out for each channel in parallel columns the data recorded in successive entries. A typical print-out is reproduced in Figure 6. The first column is an arbitrary run number, assigned by the IBM printer to successive entries on the tape. The next two columns are the date and time. Channel number 0 was used at first for the Barton instrument and later for a diagnostic entry of a zero or constant voltage, after the Esterline Angus troubles became chronic. The next three columns were used for Bendix

Figure 6

DAILY PRINT-OUT

```
                         CHANNEL   NUMBERS
---------------------------------------------------------------------------
      DAY   HR        0      1      2      3      4      5      6
      ---   ---     -----  -----  -----  -----  -----  -----  -----

163   219   1545     0.0
164   219   1550     0.0    54.0   78.9    8.7    0.0    0.1   24.1
165   219   1555     0.0    53.6   79.2    8.3    0.0    0.1   24.3
166   219   1555     0.0    53.8   79.0    8.4    0.0    0.1   24.1
167   219   1555     0.0
168   219   16 0     0.0    54.2    1.4    7.6    0.0    0.1   23.3

169   219   16 5     0.0    55.5    0.4    7.3    0.0    0.1   23.0
170   219   1610     0.0    55.3    0.2    7.2    0.0    0.1   22.8
171   219   1615     0.0    54.8    0.0    7.3    0.0    0.0   23.1
172   219   1617     0.0
173   219   1617     0.0
174   219   1620     0.0     0.0  107.1    0.3    0.0    0.1   14.0

175   219   1625     0.0     0.0  103.1    0.2    0.0    0.1   11.1
176   219   1629     0.0
177   219   1629     0.0
178   219   1630     0.0     0.0  105.6    0.3    0.0    0.0   15.9
179   219   1635     0.0    51.1    0.5    3.1    0.0    0.1   22.6
180   219   1640     0.0    51.3    0.1   -0.2    0.0    0.1   21.6

181   219   17 0     0.0    50.4    0.0   -0.5    0.0    0.1   15.2
182   219   1720     0.0    49.5    0.0   -0.5    0.0    0.1   14.2
183   219   1740     0.0    48.4    0.0   -0.3    0.0    0.1   10.5
184   219   18 0     0.0    47.6    0.0   -0.5    0.0    0.1   10.4
185   219   1820     0.0    47.6    0.0   -0.5    0.0    0.1   10.7
186   219   1840     0.0    47.2    0.0   -0.3    0.0    0.1    9.4

187   219   19 0     0.0    47.1    0.0   -0.7    0.0    0.1    9.8
188   219   1920     0.0    47.3    0.0   -0.6    0.0    0.1    9.1
189   219   1940     0.0    46.8   -0.1   -0.5    0.0    0.1    7.9
190   219   20 0     0.0    46.2    0.0   -0.6    0.0    0.1    7.7
191   219   2020     0.0    47.2    0.0   -0.8    0.0    0.1    8.1
192   219   2040     0.0    47.7    0.0   -0.7    0.0    0.1    7.3

193   219   21 0     0.0    47.7    0.0   -0.6    0.0    0.1    6.1
194   219   2120     0.0    47.2   -0.1   -0.8    0.0    0.1    7.2
195   219   2140     0.0    47.5   -0.1   -0.9    0.0    0.1    6.5
196   219   22 0     0.0    47.4    0.0   -0.8    0.0    0.1    4.9
197   219   2270     0.0    46.0   -0.1   -0.7    0.0    0.1    4.2
198   219   2240     0.0    46.1   -0.1   -0.7    0.0    0.1    3.0
```

note the peak on #2 (COS) ~ 15 min. delay
#1, #3 return to pre-scrubber level
#3 (SO2) – leaves 15% unscrubbed

COS off

Now COS only, no scrubber

the reading is not H2S or SO2 ? ; also #1 ~ #3,
in the chart

(continue)
→ COS off : 300 a H2S + [illegible] flow, [illegible] air
purges some SO2 from scrubber in first cycle (73→21),
but not COS (105→.5) ; ∴ [illegible], [illegible]...

the electrolyte is apparently n.g., after COS cycles.
#1 bubbled at 11-18, then → 3

channels 1, 2 and 3, which were set for various gases during the program depending on the GC column in use. Channel 4 was used for the Houston Atlas, 5 for the RAC, 6 for the Barton, and other channels as needed for the Dohrmann or auxiliary equipment. Negative entries were printed as read, usually as small values during zeroing. A consistent column of negative values appears for the RAC when it is set to record tape absorbance by difference, rather than transmission.

Program 3 computes the mean and standard deviation for any number of columns and entries, up to 60 per column. Instruction cards for this computation are made out after inspection of the print-out from Program 1A. This calculation usually includes all entries between those selected. It can also specify taking every nth entry, to cover a longer period of time, or to pick out readings for the RAC at a 10 minute or longer period while the other instruments are being read every 5 minutes.

Program 2 is a special computation of the RAC absorption curve, which can reproduce the whole curve from a set of three to five points at regularly timed intervals. This computation was demonstrated but not much used, since it requires taking and processing data at intervals more frequent than those necessary for the other instruments on test. It can be replaced by the linearizers available as standard equipment in other units, such as the Tracor 250H.

The printed tape on the Esterline Angus and the chart record on the Barton are both convenient places to record changes in sample, processing, or instrument scale setting. The Houston Atlas recorder chart was not adequate for this purpose. Records from the lab notebook and charts were entered on the daily print-out as shown in Figure 6, during periods of satisfactory operation, for the interpretation of data and selection of entries for computations.

2.4.3 Linearity of Scales

The instruments on test did not give readings suitable for direct output in concentration, or for computer conversion of the raw data from MV observed to calculated ppm. The principal reasons for this were the unpredictable variations in zero values for the Barton, by day and by attenuation scale, and for the Houston Atlas and RAC for each new tape. The RAC system to correct for tape zero required an excessive amount of maintenance to keep it in operation at a high rate of tape feed. When it did work, the instrument span and the placing of the data on the logarithmic output curve were changed by the automated zero shift. The Bendix zero was inherently more stable, but its linearity is limited at increasing concentrations, and each change in GC packing or in gating for a new set of GC peaks requires a new calibration curve.

2.4.3.1 Barton Calibration Curves

The linearity of response of the Barton Titrator over concentrations differing by 10^4 or more is a distinct advantage. It was used for this reason as an intermediate reference in this program, to extend the range and volumes of calibration gas blends matched against permeation tubes or known small synthetic samples. Since we were dealing with known blends or pure compounds, the variable response of the Barton to different compounds could be allowed for, and did not constitute a problem in calibration. The conversion factors supplied with the instrument do not fall exactly on a smooth curve, however, and various efforts to provide a better set of values have been reported in the literature.

The handbook data are plotted in Figure 7. Both the attenuation scale and the response scale are logarithmic, and the values reported for five sulfur types are all close to a straight line with a slope of 1. Deviations from the line are greatest at the lower attenuations. Experimental values as determined by various authors and modified for use in this report are given in Table 4. The ranges given by Cooper and Rossano(4) refer to different detection cells, which they note should be calibrated individually for accurate results. Their values are not based on all the information available, however, since their ranges do not include three of the seven factors in the Barton handbook.

A more consistent set of factors can be generated by treating the values for each compound at different attentuation scales as a single set of data, and constructing a faired curve by standard regression analysis. Adjusted values are shown in Table 4 for the H_2S factors of the Barton handbook, and Blosser(5). Details of the Barton calculation are shown in Appendix II: it is apparent that the value of .023 at x.3 is suspect and should be discarded. A modified faired curve constructed without it leaves the values at x1 and x.1 close to the unit level, for which the instrument was originally designed. Preferred values as used in this report are based on this modified curve.

Figure 7

BARTON CONVERSION FACTORS

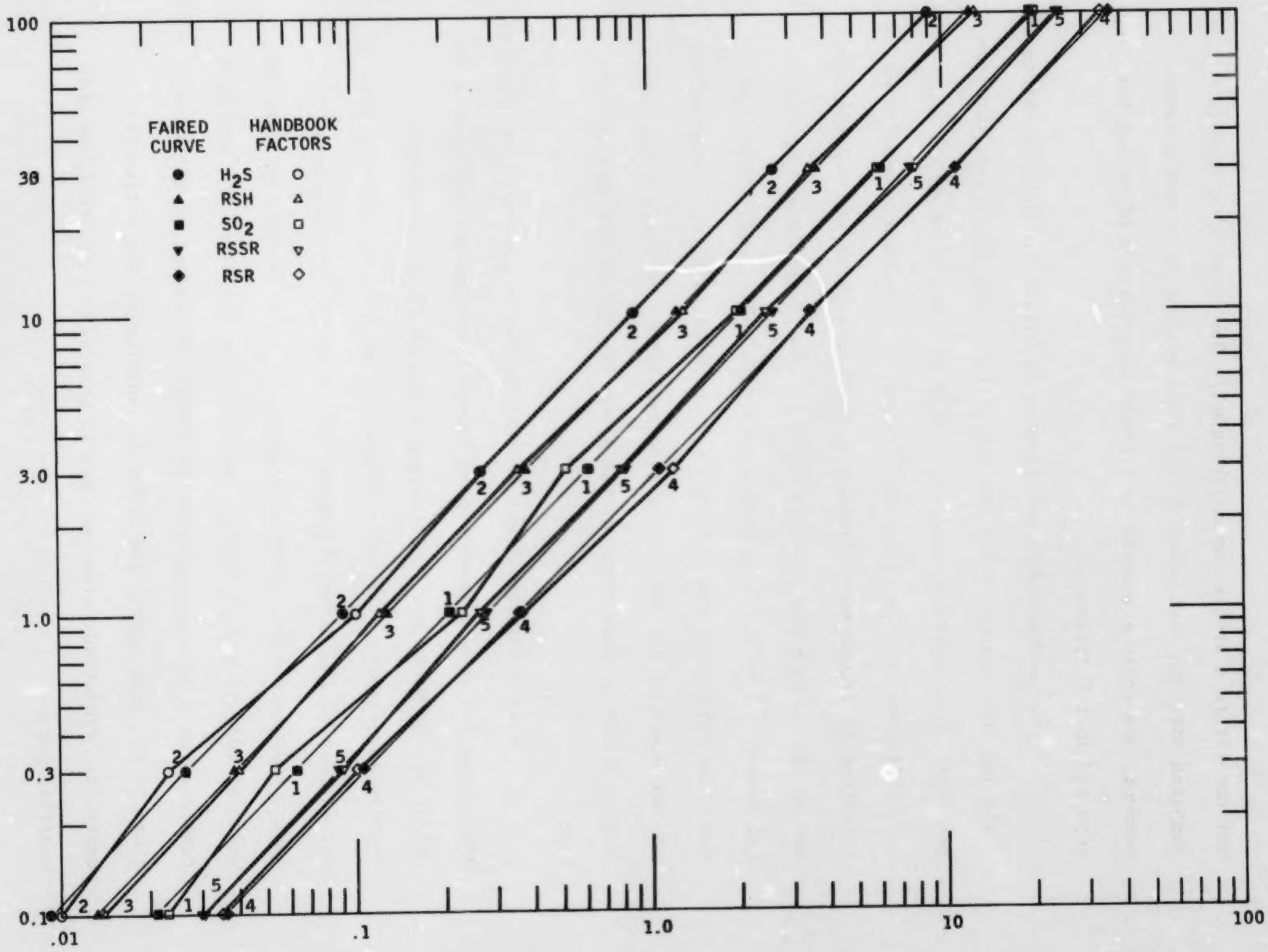

TABLE 4

BARTON TITRATOR

Attenuation Range	H_2S Conversion Factors (x MV Scale Reading = ppm)						
	Preferred Values	Barton	Blosser + Cooper	Cooper + Rossano	Faired Curve		
					Barton	Blosser	Modified
x .1	.010	.010	.013	.008-.013	.009	.012	.010
x .3	.029	.023	.033	.030-.035	.027	.034	.029
x 1	.095	.10	.110	.09-.12	.091	.103	.095
x 3	.28	.27	.25	.24-.26	.269	.284	.278
x 10	.90	.86	.80	.7-.9	.890	.867	.904
x 30	2.6	2.6	2.4	1.5-2.5	2.66	2.40	2.64
x100	8.6	9.0	8.0	4.5-9.0	8.80	7.32	8.60

All three of the sets of experimental factors reported in Table 4 show a discontinuity in the values reported above and below the x3 and x1 range. This is illustrated in Figure 8: a line drawn between these two factors extrapolates consistently below the experimental values for lower ranges, and above the experimental line for higher ranges. This corresponds to a dividing point in the performance of the Barton cell: it equilibrates within 2 minutes or less at the x3 scale and above, and much more slowly at x1 and below. Directionally, any experimental reading which had not been allowed to equilibrate fully at the lowest attenuations could be translated into a pseudo-factor which is too high. The uncertainties observed in all factors were greatest at the x1 scale and below, which are used only for ambient measurements.

The factors given for SO_2, CSH, CSC and CSSC in the Barton handbook are accepted by Blosser. Faired curves calculated for these show a consistent relationship for the data as a whole. The equations for these curves are given in Table 5, with original and adjusted values for the factors at each attenuation. The low-level delayed response to CS_2 encountered in this project is not noted in these references.

2.4.3.2 Bendix

Linearity of the Bendix instrument for a given sample size is related basically to the limits of the FPD sensor and to the chemistry of the sulfur compound reactions in the hydrogen-rich flame, as shown above in Figures 3 and 4. The plots of Bendix readings vs Barton values show linear correlations within $\pm$ 3% for H_2S through about 80 ppm. Similar data are given in Section 3 below for SO_2 and CSH through 80 ppm, and for COS through 30 ppm.

Figure 8

DISCONTINUITY IN H_2S FACTORS

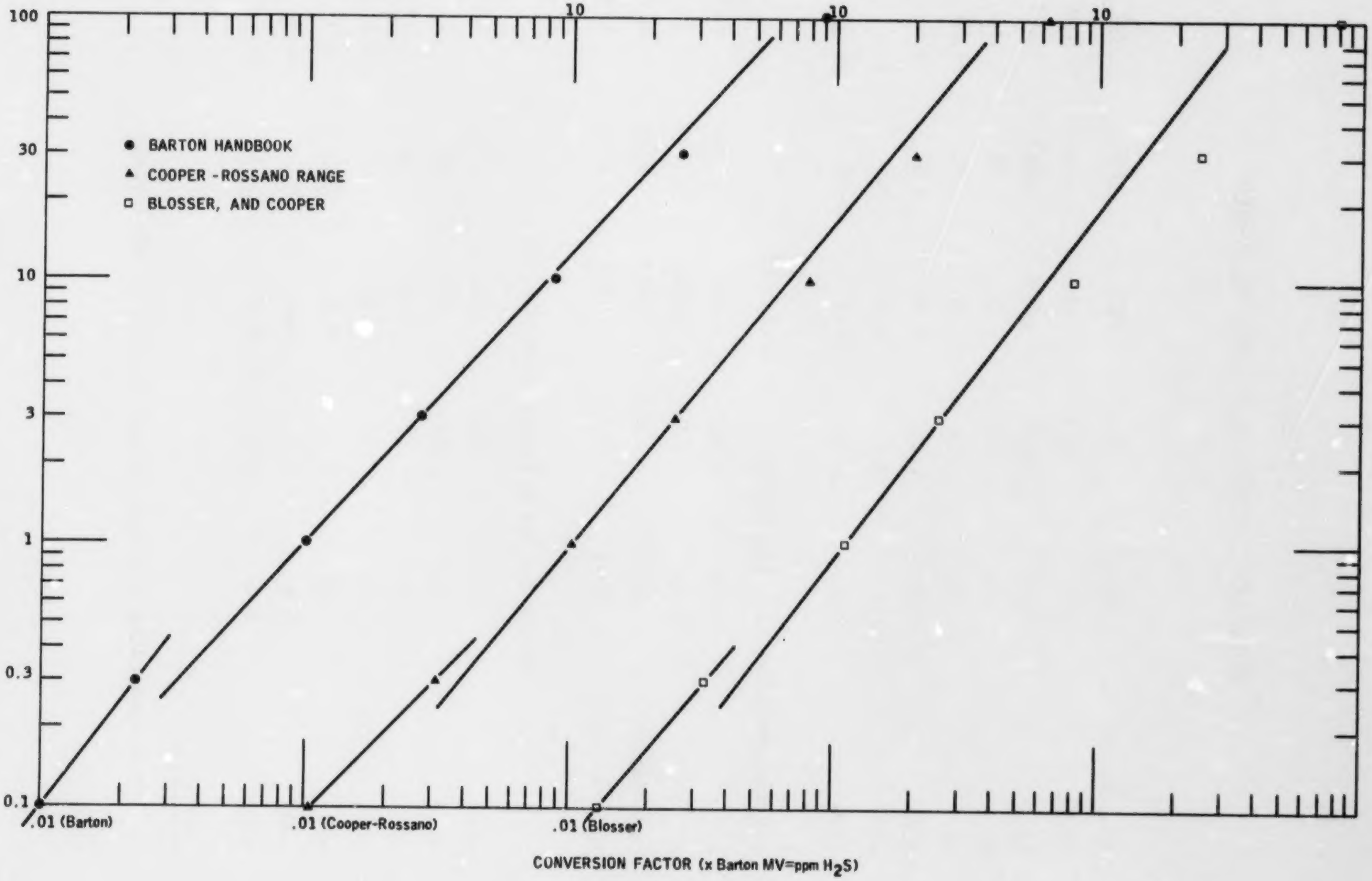

TABLE 5

NORMALIZED CONVERSION FACTORS FOR BARTON

Scale	H_2S*	CSH	SO_2	CSSC	CSC
x0.1	.010	.013	.021	.030	.035
x0.3	.029	.039	.063	.087	.107
x1	.095	.128	.21	.28	.36
x3	.28	.38	.62	.81	1.08
x10	.90	1.25	2.05	2.6	3.6
x30	2.6	3.7	6.1	7.6	10.9
x100	8.6	12.1	20.3	24.6	36.5
Log-log equation (A x log factor = log scale -B)					
A	1.022	1.012	1.005	1.029	.9954
B	1.0448	.9032	.6861	.5692	.4446
Std. Error	.0203*	.0308	.0427	.0230	.0272
Correl. Coeff.	.9993	.9997	.9993	.9998	.9997
Barton Handbook Values (Unmodified)					
x0.1	.01	.014	.023	.031	.035
x0.3	.023	.04	.053	.09	.1
x1	.10	.12	.23	.26	.37
x3	.27	.35	.62	.8	1.2
x10	.86	1.3	2.0	2.5	3.5
x30	2.6	3.5	6.0	8.0	11.0
x100	9.0	13.0	20.7	25.0	35.0

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* After discarding reported factor for H_2S at x0.3 scale.

2.4.3.3 Houston Atlas and RAC

The linearity of the Houston Atlas sensor at ± 3% is better than the inaccuracies due to unevenness in the tape, at ± 5 to 10%. The simple timing sector gives dilution values which are reliable as far as 10:1, but increasingly less so at values of 20:1 or higher. An optional system provided for dual dilution which sends an extra pulse of hydrogen into the lines along with the timed sample pulse gives non-linear results, probably due to the interrupted flow. This system was not used, and is not recommended. A microliter injection system is now available, designed for liquid samples, which can be adapted for gaseous samples at high dilution. The 1973 model of the Houston Atlas tape sampler has gone to a measurement of slopes instead of direct scale readings. This should extend its useful range, as well as decreasing its sensitivity to differences in the tape. The logarithmic response curve of the RAC sampler and the necessity to consult a conversion chart to get even a qualitative result are distinct disadvantages compared to the other instruments.

2.5 Equipment Van

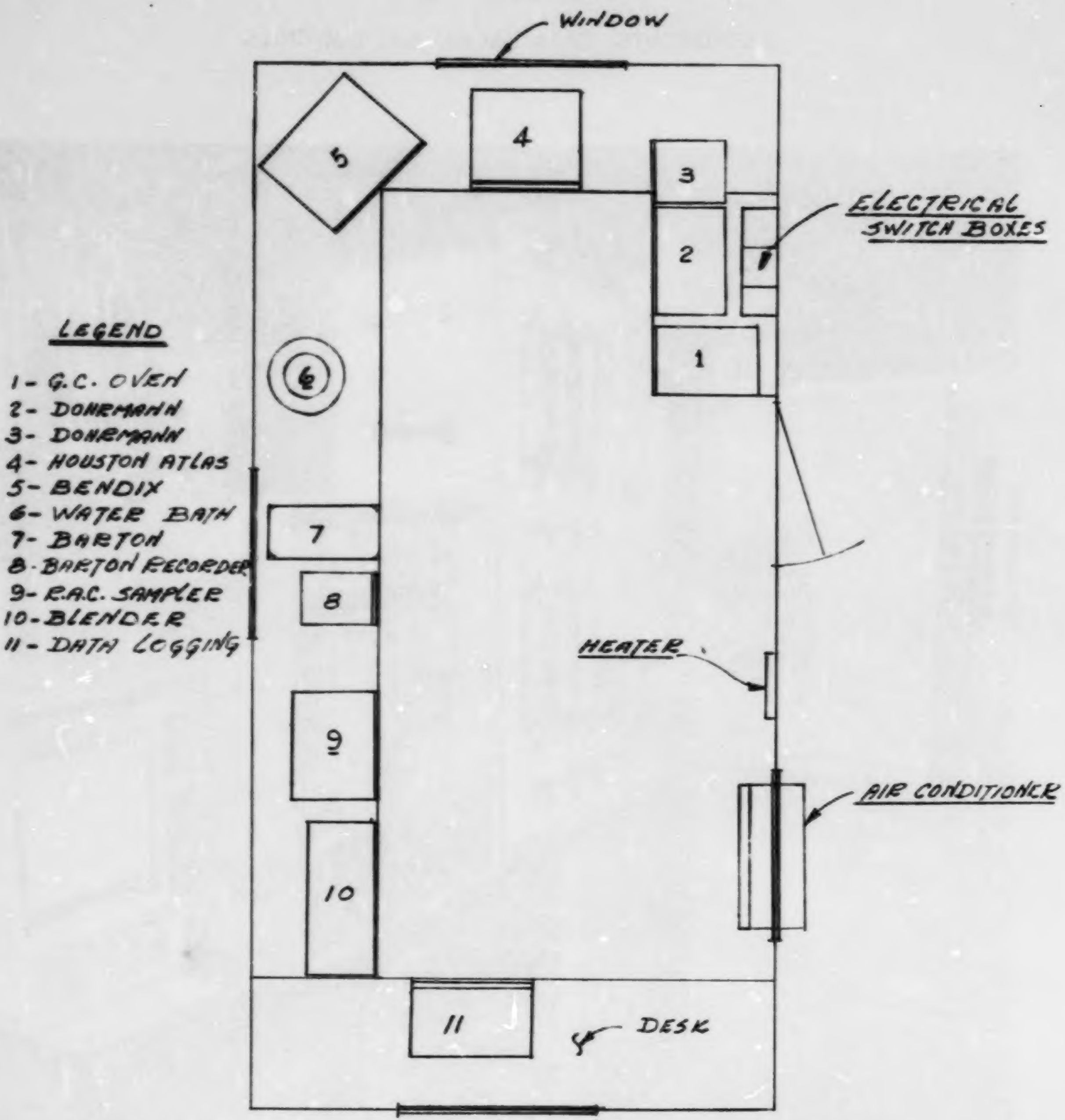
For the field test program all instruments, calibration systems and gas manifold controls were mounted in a mobile air-conditioned equipment van. This was a standard production model 8' x 20' office-type trailer, Model M20 from the Coastal Mobile and Modular Corporation. The complete sampling console for the probes, filters, blow-back system, knock-out traps, pumps and accompanying valves was mounted at the stack. This was at the 50' level 100' horizontally from the van location in the refinery, at a 100' level 30' from the van at the paper mill recovery stack, and at a 20' level next to the van at the lime kiln stack. A suitable length of electrically heated 3/8" Teflon line led from the console to the refrigerator at the trailer van. Power controls for the heated line were placed in the van.

Satisfactory operation was achieved with gauge pressure in the range of 10 to 15 psig at the sampling compressor outlet, and a total sample flow of two to four liters per minute. The Hankinson refrigerator unit had a cyclone separator chamber to drop out any water separated promptly, with a minimum of subsequent gas contact. The amount of water separated out here at 40°F was normally about 30 cc in 16 hours, overnight, or 0.1 mol per hour. This is equivalent to 2 volume % of water removed, at a sample flow of 2 liters per minute. The rate of sample flow, the use of a heated line, and rapid chilling and separation were sufficient to avoid any evidence of sulfur formation or dissolved SO_2 in the refrigerator trap.

The interior layout of the trailer van is shown in Figures 9, 10 and 11. Gas from the refrigerator mounted under the van passes up into the gas blending control box for the manifold system, diagrammed above in Figure 1 (Section 2.3.1). Either charcoal filtered plant air or cylinder air may be used for sample dilution, or a calibration gas can be used for dilution if desired. The sample and dilution gas streams were each supplied by a bank of three rotameters in parallel, to cover the range from 10 cc to 4000 cc per minute. Smaller amounts of calibration gases were fed directly to the gas manifold after the

Figure 9

ODORANTS VAN LAYOUT


WINDOW
5
4
3
2
1
ELECTRICAL SWITCH BOXES
LEGEND
1- G.C. OVEN
2- DOHRMANN
3- DOHRMANN
4- HOUSTON ATLAS
5- BENDIX
6- WATER BATH
7- BARTON
8- BARTON RECORDER
9- R.A.C. SAMPLER
10- BLENDER
11- DATA LOGGING
6
7
8
HEATER
9
AIR CONDITIONER
10
11
DESK

ODORHNTS VAN LAYOUT.

Figure 10

VAN INTERIOR, FRONT

INSTRUMENTS, DATA RACKS, GAS CONTROLS

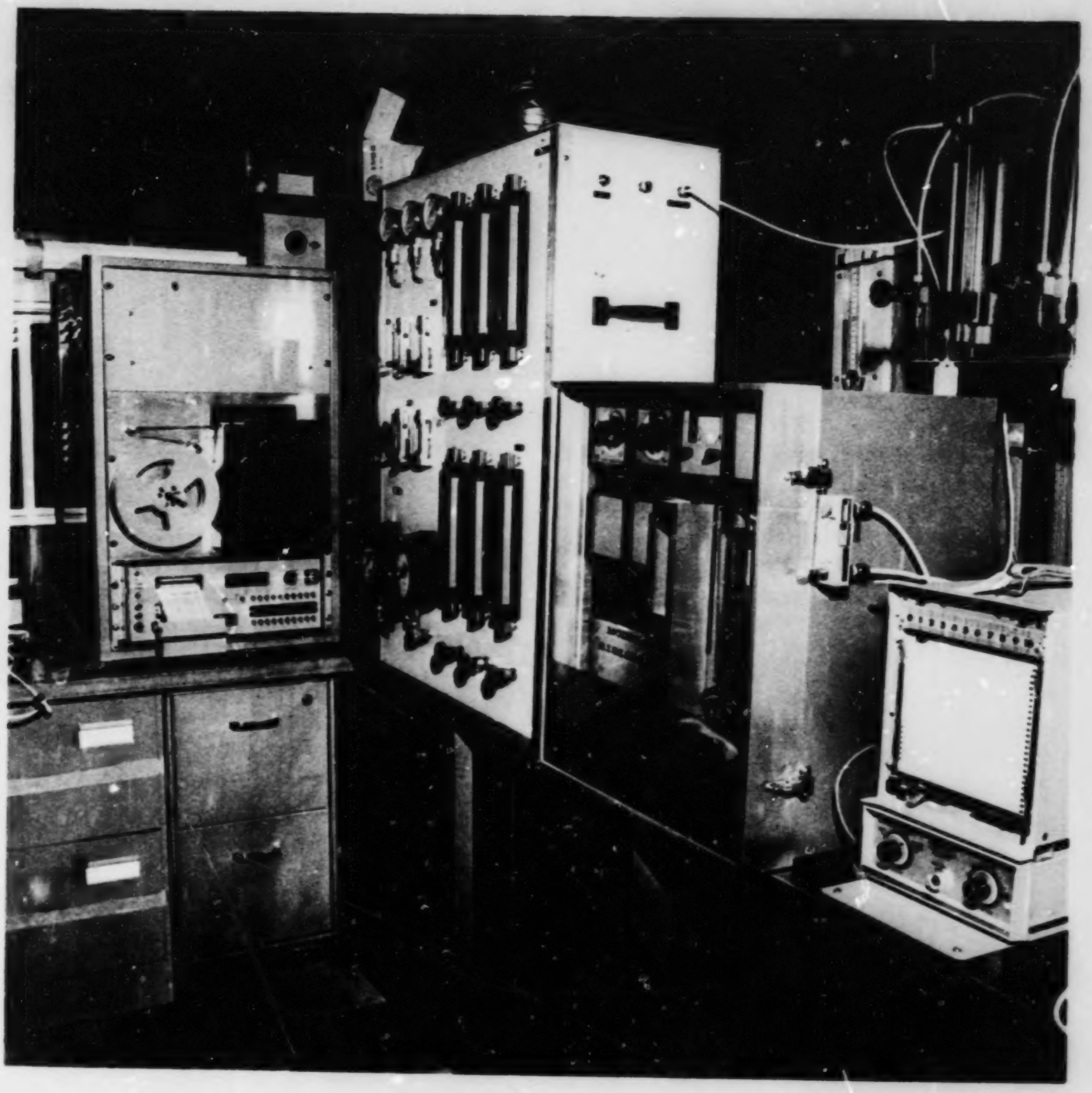
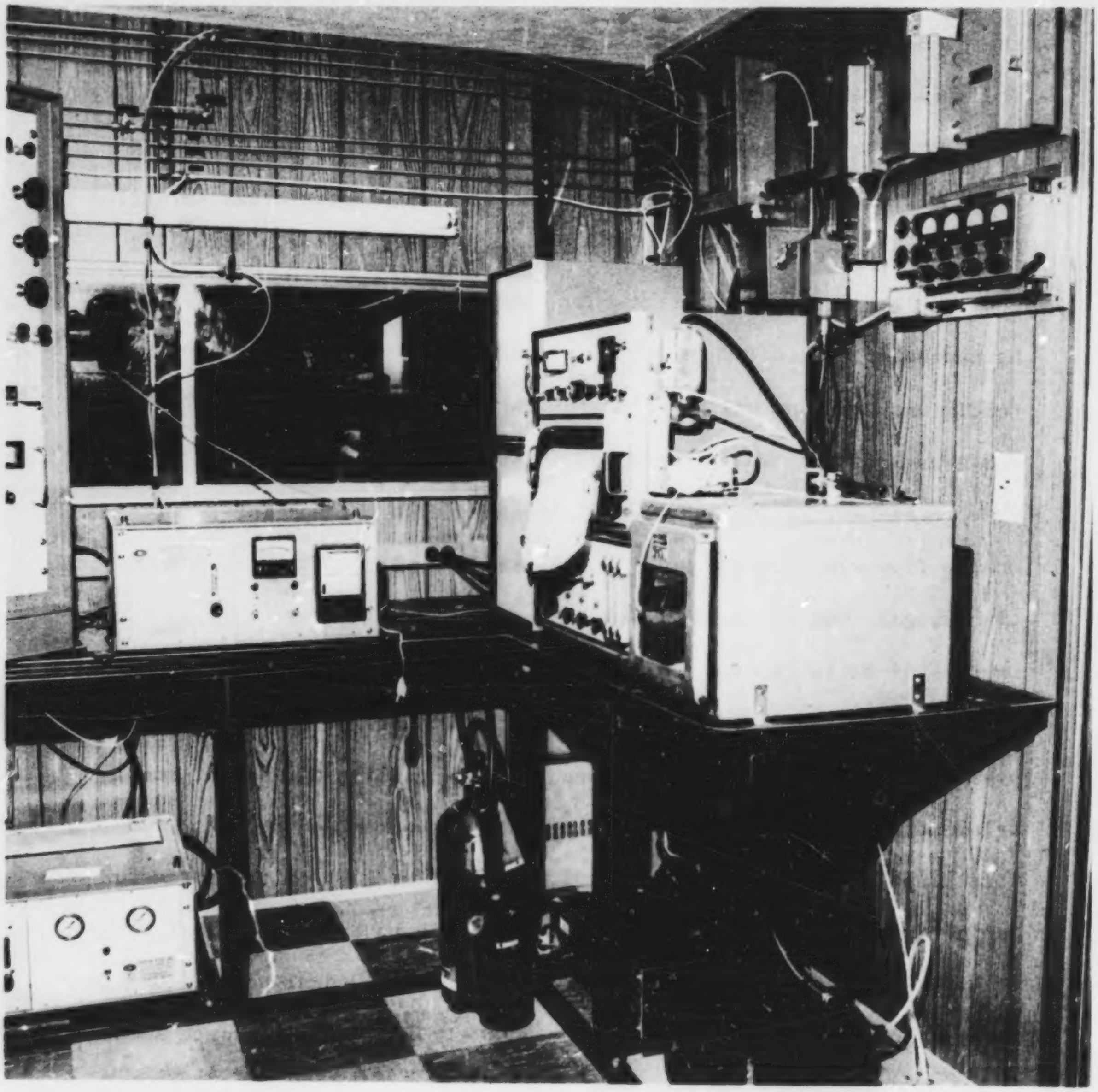


Figure 11

VAN INTERIOR, REAR

INSTRUMENTS AND ELECTRICAL CONTROLS



blender, through a bank of three mass flow meters. These were calibrated for accurate metering of 1 cc to 100 cc per minute of dilute gas blends in nitrogen. The total gas supply from the blender to the manifold could be passed through a permeation tube cell in a water bath, or the permeation cell could be put in the line from the manifold to individual instruments to get a higher gas concentration.

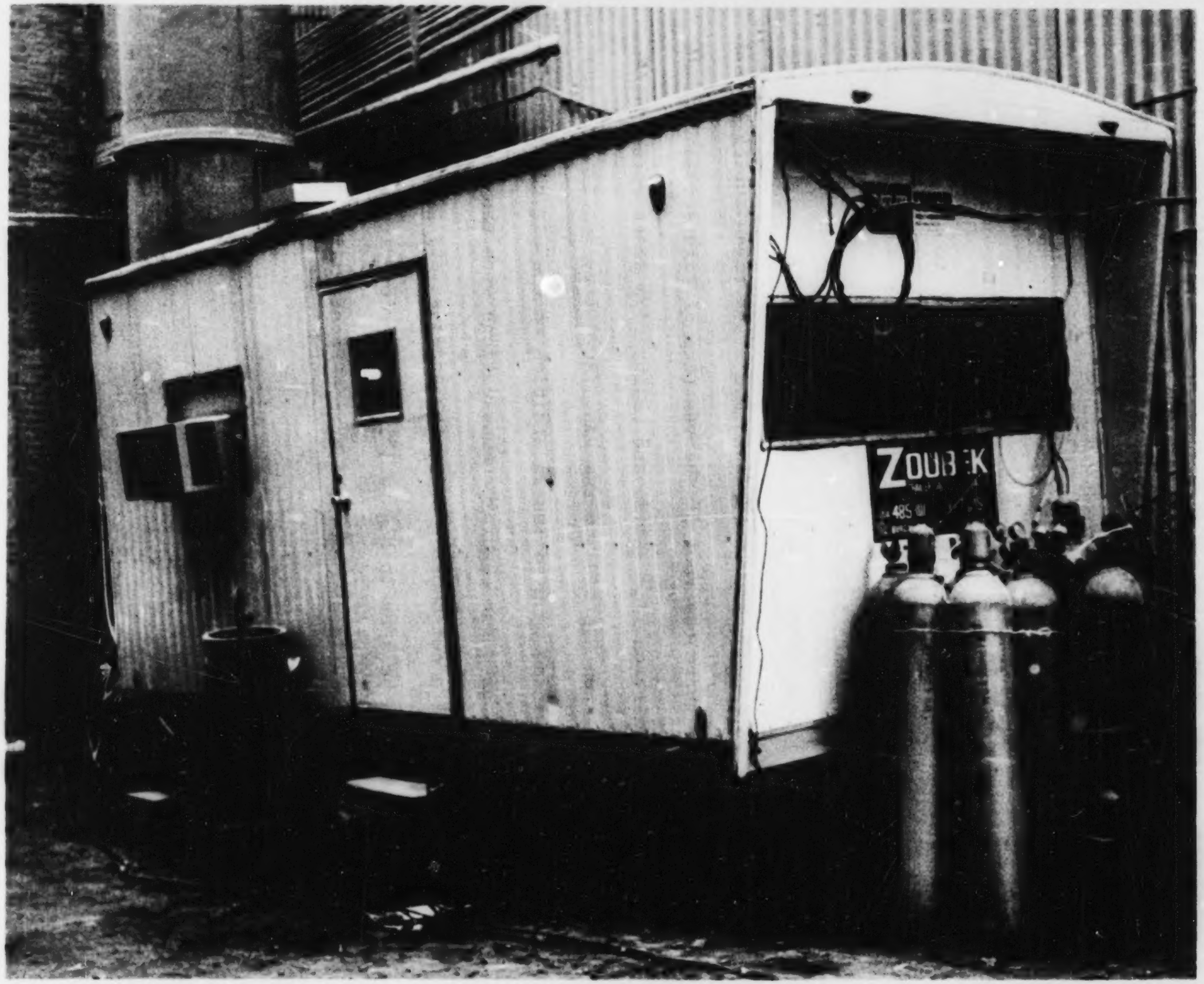
The gas manifold pressure was held at a constant 108 mm of Hg (± 0.5 mm), equal to 2.09 psig. Gas from the manifold was throttled down to atmospheric pressure by individual needle valves controlling the sample feed to each instrument. This was monitored by an open-end Hg manometer controlled to ± 1 mm at each instrument for feed to the Barton, Bendix and Dohrmann cells. The Houston Atlas pump which was disconnected for these tests normally comes before the instrument and flow is controlled by a rotameter, against the normal pressure drop through the instrument. Sample flow was normally held at full scale of 0.3 CF/hr plus 0.3 CF/hr of hydrogen, but it could be cut to e.g., 10%, 20% or 40% of F.S. for samples of variable high concentration. Flow through the RAC was controlled by aspirating dilution air or cylinder gas at atmospheric pressure through one end of an open T, while pulling a constant small volume of sample through a rotameter into the other end of the T. This dilution was controlled to 10%. 20%, 40% or 100% of the rotameter scale of 0.9 CF/hr. The RAC calibration scale covers the nominal range of 0.001 to 0.1 ppm of H_2S in a 15 cu. ft. sample, equal to 0.25 CF/min for one hour. This gives a factor of 200 to 2000 for a 5 minute sample at 10% to 100% of the rotameter setting, or an upper range of 2 to 200 ppm. Lower ranges are covered by lengthening the cycle time to 10 minutes or longer multiples of 5 minutes, as desired.

Instruments were arranged on benches around the interior of the van, as shown in Figure 9. The Esterline Angus and Tally Paper Punch were rack-mounted on the records desk, next to the blending control box. An interior view of this end of the van with the RAC and Barton instruments is shown in Figure 11.

All vent lines from the blender, manifold, and individual instruments were conducted inside a common stack to an outlet extending three feet above the roof of the van (top of Figure 10). Storage cylinders for air, carrier gases, and calibration gases were chained in racks mounted on the side of the van. Auxiliary ventilation was supplied by a window mounted fan in addition to the air conditioner. A telephone was used for regular communications with the office or a plant foreman in a neighboring unit, for added safety precaution. These arrangements can be seen in Figure 12, an exterior view of the van on site, at the lime kiln stack of the Warren Paper Mill.

Figure 12

EQUIPMENT VAN ON SITE



3. PERFORMANCE OF INSTRUMENTS

3.1 Response Times and Zeroing

3.1.1 Barton

The Barton coulometer shows an initial response to changes in sample concentration within a few seconds and can travel full scale in 10 seconds or less, at its higher scale ranges. This intrinsic speed of response is an advantage which is not commonly utilized in plant practice, however. It accentuates a very short-time variability of readings and zero levels which is related to the hydraulic properties of the cell. This instability appears as a restricted fluctuation, between limits which are related to the rate of generation of titrant bromine in the cell and the rate at which excess bromine is stripped out by the constant flow of carrier gas. The rate of fluctuation is determined by the circulation of electrolyte within the Barton cell, which depends on a gas lift effect of the sample gas and a "wiggler valve" between cell chambers. Coulometric cells in the Philips SO_2 Monitor and the Dohrmann Microcoulometer are provided with a more positive circulation of electrolyte, and they do not show the same instability. Laboratory experience with Dohrmann cells shows that improved stirring is directly related to stability of output.

This short-term instability is more of a hazard in electronic data logging than it is in a visual record. The variations concerned take place within a few seconds, and their apparent effect is minimized by running the recorder at a low chart speed. This produces a record in the form of narrow band, instead of a moving line. The width of this band varies with the hydraulic properties of the cell, and for any cell its width is inversely related to the attenuation scale. The uncertainty which it introduces appears both in zeroing and in sample readings. The average effect is given in the Barton manual; selected cells do better than this, and a noisy cell does not do as well.

TABLE 6

BARTON RECORDER ZERO LEVEL RANGE % OF FULL SCALE, AT 250 cc/min. FLOW

Range Switch Setting	Blank Level (Instruction Manual)	Typical Averages Observed
.1	20 ± 8	
.3	12 ± 4	15.6
1	6 ± 3	8.9
3	3 ± 1.5	4.4*
10	2 ± 0.5	2.2
30	1.5 ± 0.8	1.3
100	0.7 ± 0.4	1.2

---

* Daily averages (and standard deviations) at x3 on successive days = 3.5 (± 0.3), 4.1 (± 0.3), 5.4 (± 0.4).

The ± values in this table represent expected deviations from the mean in any instantaneous reading, not just an uncertainty in the average value.

The Barton commercial unit allows for this effect essentially by visual averaging. This also has another purpose. The compositions of stack gases from a paper mill recovery furnace and from other large combustion units are subject to rapid fluctuations in concentration, within a few seconds, whose effect is averaged as soon as they reach the atmosphere. For most environmental studies, therefore, the analysis is better averaged than recorded in detail. The standard

Barton procedure recommends a mechanical averaging which masks the intrinsic speed of response, by placing a one liter surge pot in the sample line(6). This serves as a trap for any water and particulates condensed in the line, but it also imposes a time delay of about 15 minutes in full response. The standard gas flow rate is 250 cc/minute, which would give a plug-flow time of 4 minutes for one complete gas exchange. The experimentally observed time interval of 12-15 minutes for a full response with the surge cell in line corresponds to an exponential decay curve, to allow for dilution and mixing. This is a good check with theory, which should require 3.3 times the plug-flow time to achieve a 99% exchange of gases. The instrument tests in this program were run without the surge cell; this is also common practice in paper mills when the Barton is being used for process control studies.

For a better understanding and diagnosis of cell behavior and instrument limitations, the recorder was run at a more rapid chart speed of 30 inches per hour during initial laboratory evaluations, instead of the normal 2 inches per hour used for field tests. At the slow chart speed, it became apparent that the variations in cell reading are not in fact random variations about the mean, but are a bipolar distribution within limits. This appears in the statistical analysis of data as a normal distribution of data at the 1 σ level, but a much higher fraction of data points than expected fall within the 2 σ limit. The effect is clearly illustrated by typical chart traces at different attenuations, as shown in Figure 13.

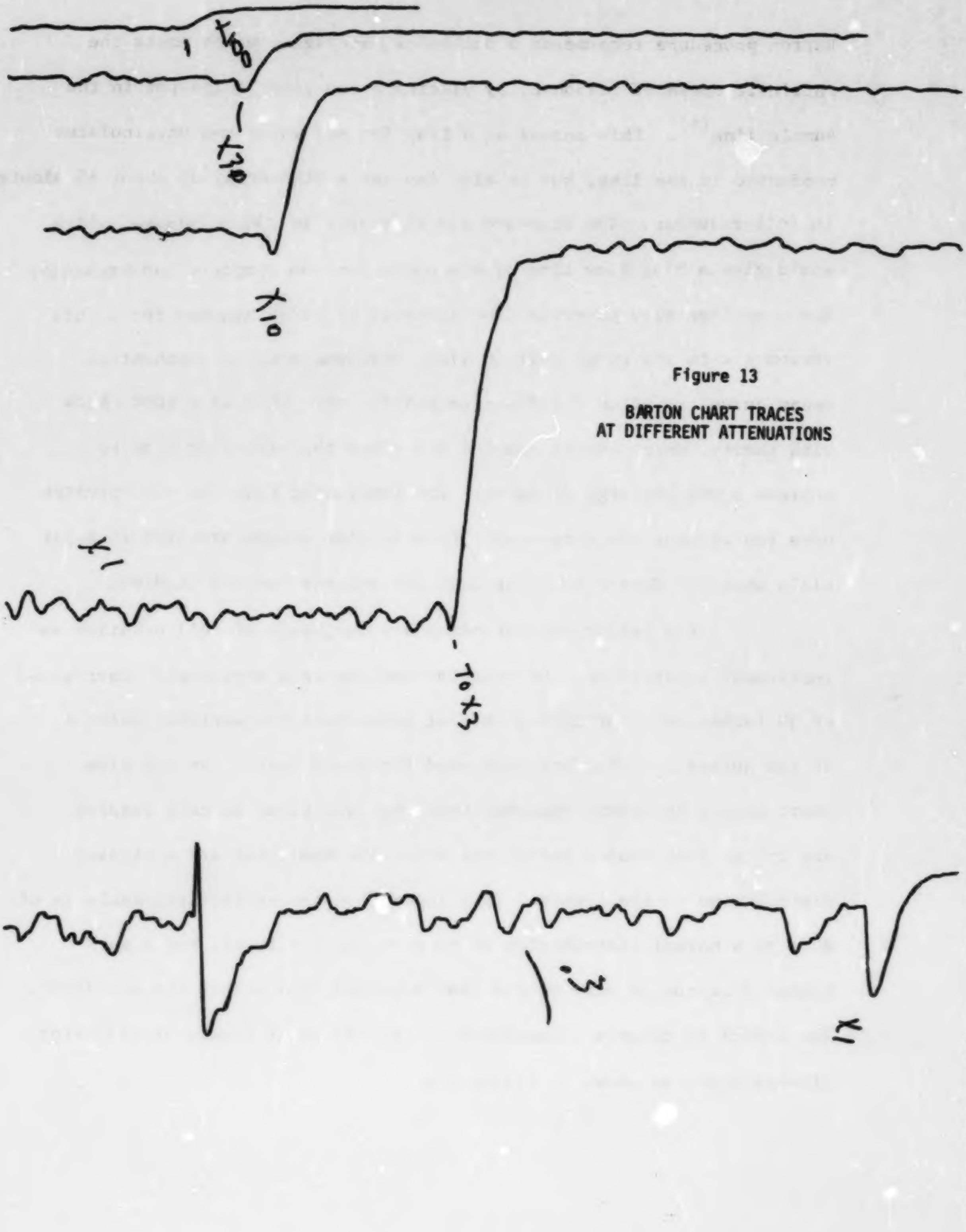


Figure 13

BARTON CHART TRACES
AT DIFFERENT ATTENUATIONS

Figure 13 also shows the effect of scale on band width. Plant operators using the Barton instrument normally operate it at the x10 scale (or higher) which minimizes the visual effect of the instability discussed above, and gives more nearly a straight line on the chart. Electronic averaging of the signal from the cell over a period of 30 seconds to a minute might be used to give a smoother output for data logging.

The Barton cell zero also shows a continuous short-term drift over a period of a day or less, which requires at least daily re-determination. This can be a serious disadvantage. The zero blank,like all sample readings, is a dynamic balance involving the small amount of titrant bromine stripped out of the electrolyte by carrier gas, and the current required to keep the concentration of free bromine available in the cell at a constant level. This zero varies with changes in barometric pressure, temperature, the condition of the electrolyte, and above all with small changes in the "constant" flow rate of total gas. The uncertainties in zero level which this represents fall within the same limits as shown in Table 6, since they are related to the same dynamic balance within the cell, but in this case it is the average which is shifting within the limits shown. The lack of an absolute zero means that all measurements are differential values, subject to an uncertainty of 1/2 to 3 units on scale. This uncertainty varies with attenuation, and the length of time since the last measurement of the zero blank.

A cumulative anomalous effect of CS_2 on cell zero was observed on continued exposure at ppm levels. Apparently CS_2 is only partly oxidized and builds up slowly to poison the cell response, until it is stripped out by a clean carrier gas.

It should be noted that these difficulties with zero level are not unavoidable in coulometric titrations, at ambient levels. Most of them have been corrected in the Philips SO_2 Monitor by using a thermostated cell, with stirring and more positive flow control, and an internal calibration unit for automatic re-zeroing on demand.

3.1.2 Bendix

The GC/FPD combination in the Bendix Chromatograph is much better in zero stability than the other instruments on field test, by an order of magnitude. Its normal zero variation was less than 0.5 scale unit, with a standard deviation of 0.1 or 0.2. This held stable for the first 6 months on test.

Stability was not as good after shipment from New Jersey to Maine in a trailer van without factory readjustment, after which the standard deviation on zero level was about 0.2 to 0.4. This was still superior performance, by comparison. The instrument is provided with two systems for adjusting zero level, either automatically each cycle or on demand by a manual control. Rebalancing the automatic zero when it is out of adjustment requires circuit testing equipment, and it was not attempted in the field. The manufacturer has redesigned this automatic zero system during 1972 to make it more stable and easier to adjust. The need for this change was further confirmed by the return trip from Maine to New Jersey, when the automatic zero adjustment became inoperative and the manual setting for electronic zeroing was actuated daily, or as required.

Response time in the Bendix is normally 98% in the first or second 5 minute cycle, depending on exactly when in the GC cycle the change in concentration to be measured occurs. This is not affected by large changes in concentration, as long as the gas components remain the same. Exceptions may occur when one component has been absent (such as CSH) with a large excess of others (H_2S and SO_2), requiring a third cycle to get full response. This depends upon the GC packing.

Response to changes in attenuation scale are immediate and arithmetic, up to where the instrument goes off scale. An automatic attenuation subsystem is provided but it was found to give a different zero level at different attenuations, and was not included in the laboratory evaluation. This sub-system was apparently no longer balanced properly with the rest of the system after the GC columns were shortened to 20% of their original length, which was done at the start of the test program to increase the instrument range. It operated satisfactorily in field tests for differential measurements, and in making matched synthetic blends to duplicate selected stack gas analyses. Rebalancing it is a factory operation, and the lack of the automatic feature did not interfere with operations at a constant attentuation scale.

3.1.3 Houston Atlas

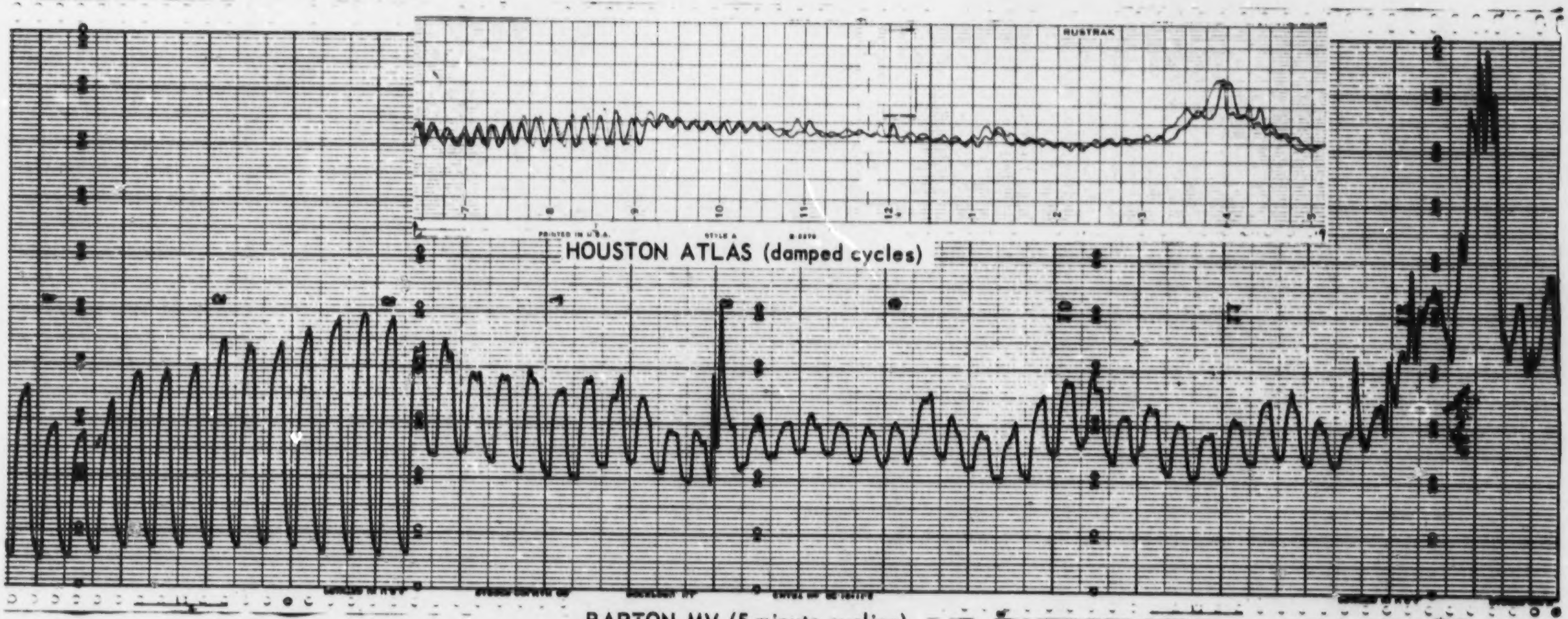
Zeroing in the Houston Atlas tape recorder is an approximation achieved by a simple screwdriver adjustment, to allow for the average reflectance of the unexposed tape and subtract it mechanically from the recorded sample readings. This average must be reset for each tape, and it varies by ± 3 to 5 percent for a given tape. Overnight runs regularly show occasional spikes of -10% or more in reflectance, due to tape unevenness which is greater than average.

The combination of the Model 825 tape recorder and the pyrolytic/catalytic converters in the Model 855 unit on test gave a critically slow response time, on the order of 25 minutes. This interfered seriously with instrument evaluation. Several factors were apparently involved: one was the volumetric effect of the enlarged pyrolytic and catalytic conversion chambers, which create the same type of gas mixing and dilution delays as the gas surge pot in the Barton Titrator. This effect was confirmed at one point in the field tests when one of the two Barton probes slipped its timing adjustment and began to blow air back into the line every other 5 minutes on alternating with the second probe, which was providing stack sample gas. This gave a sawtooth reading on the Barton,shown in Figure 14. The minimum Barton readings were from 80 to 90% below the maximum, approaching but not quite reaching the zero level due to incomplete air dilution between sample peaks. The Houston Atlas shows the same sawtooth effect but greatly damped, with valleys only 20% below the peaks. This pattern indicates a substantial amount of gas mixing within the instrument.

Sample adsorption on unheated metal lines within the instrument was also involved, as a time factor. The hold-up of SO_2, a highly polar gas, and heavier sulfur compounds such as CS_2 and CSSC was substantially longer than H_2S or COS, on the order of 45 minutes or more. This is

Figure 14

EFFECT OF ALTERNATING AIR BLOW IN SAMPLE LINE



HOUSTON ATLAS (damped cycles)

BARTON MV (5 minute cycling)

attributed to gas adsorption and desorption effects involving either the contact agent in the catalytic reduction chamber or the extensive amount of stainless steel tubing used to connect various reaction chambers in the instrument. The time lag for polar gases in the simple 825 recorder was from 5 to 10 minutes, instead of 25 or more.

An improved model produced by Houston Atlas during 1972 is said to cut this response time lag from 25 minutes to 4 or less by greatly reducing the free volume in the two conversion zones, and by using heated lines for all connections between the reaction chambers. No tests on this improved model were made.

3.1.4 RAC Sampler

The RAC instrument is designed with an automatic zeroing system which is intended to measure the absorbance of each spot on the tape before it is used, and reset to that zero for the succeeding measurement. The system did not work reliably, and the lack of any manual of instructions made trouble-shooting difficult. Contributing factors may have been a slow warm-up time each time the instrument was shut off to save tape, and an excessive rate of lint formation when measurements were made regularly at the minimum time interval of 5 minutes, for use at high gas concentrations. The lint production requires frequent cleaning and adjustment of the optical sensor. Both of these factors would be much less noticeable if the instrument were being used for ambient gas measurements, for which it is designed.

In ambient use the sampler can be left on stream continuously to avoid warm ups, and a time cycle of hours instead of minutes for cumulative sampling produces much less paper lint, which has to be cleaned off of optical surfaces.

The cumulative response may be read at any time but it is interpreted most conveniently against a fixed time scale, such as the 5 minutes modulus for which the instrument is set. Better results with a constant sample or a slow rate of concentration change might be obtained by measuring the rate of change of absorption rather than its absolute value, but this would not solve the problem of scale limits with rapidly changing concentrations.

3.1.5 Overall Comparison

An overall comparison of zeroing and response characteristics for the instruments on test is shown in Table 7. Preliminary laboratory results are included for the Philips Monitor which does well on this basis and for the Dohrmann cell, which responds rapidly once it is adjusted.

TABLE 7

PERFORMANCE CHARACTERISTICS
FIELD TEST RESULTS, ZEROING AND RESPONSE

	Barton	Bendix	RAC	Houston Atlas	Dohrmann Reductive	Philips
Scales used	1 to 100	50 to 2000	5 to 20 min.		200 µl	
Response time, 98% (minutes)	2	5-10	5	20-100	6 seconds	1-3
Cycle time (minutes)	Contin.	5	5	Contin.	5	Contin.
Response limits						
ppm H_2S	0.1-1000	0.05-120	.001-.15	.5-25	.005-2	.01-5
COS	nil	0.05-50	nil	.5-25	(10% of H_2S)	nil
Precision (% FS)	0.2-1.5	0.2	1-3	2-10	5	2
S.D. (MV)	0.2-0.9 0.6-1.5	0.0-0.3	1.7-3.1	1-7		
Stability of reading, % FS	0.5-2	0.2-1	2	2	0.5	1
Zero drift, % FS	3	0.5	5	5	reset	1
Automatic zero ± MV	0.5	0.2	1-2	none	none	1
Time to Failure	reset daily	10 months	2 weeks	none	reset for each sample	

3.2 Performance with Specific Gases

3.2.1 Hydrogen Sulfide

3.2.1.1 Basic Parameters

The basic parameters of linearity, accuracy, reproducibility, and equilibration time for all instruments were measured on blends of H_2S in air. Field test data on H_2S up to 120 ppm in the Bendix and Barton are given above in Figure 3. Typical data on linearity for a laboratory test run on the Barton, Bendix, RAC and Houston Atlas (Model 825) are given in Table 8. This shows the effects of concentration changes for synthetic blends of a nominal 3 to 12 ppm, and of changes in attenuation scale with a given sample.

Considering first the Barton, the precision observed is ± 4%, well within the accuracy of the gas blends. Blends of a nominal 3, 6 and 12 ppm gave a net reading on the x1 scale of 30.3, 61.1, and 127.7 MV, for observed analyses of 2.7, 5.5 and 11.5 ppm. A change in scale from x1 to x3 gave an immediate shift in MV reading from 132.9 to 59.7 MV (including zero) and a slower equilibration to 51.5, corresponding to an observed value of 12.2 ppm. A check run with a blend of 4.5 ppm (nominal) gave a net reading of 45.5 MV (x1) and an observed value of 4.1 ppm.

The same blends were checked in the Bendix alone against a permeation tube sample having a known H_2S concentration of 3.17 ppm. This gave a net H_2S reading of 19.5 MV at x500, compared to 19.4 MV for the 6 ppm blend at x1000, and 18.9 MV for the 12 ppm blend at x2000. These are check readings, showing a direct arithmetic ratio

TABLE 8

LINEARITY TO H_2S CONCENTRATION, PARALLEL TESTS
SYNTHETIC BLENDS, NOMINAL 3-12 PPM

H_2S in Air	Barton, Cell #2		Bendix			RAC		Houston Atlas
	Scale	MV (ppm)*	Scale	#1, TS MV	#2, H_2S MV	Scale	MV	(Time) to MV
3 ppm	(x1)	35.5 ± 1.7 (2.7)*	(x500)	18.6 ± 1.4	17.2 ± 0.4	(20 min.)	38.7, 39.8, 38.7 (1.7)**	(16) 6.9 (80 min.) 8.6 (0.5)
Air (zero)		5.2 ± 1.5						
6 ppm	(x1)	66.3 ± 1.7 (5.5)	(x1000)	23.1 ± 0.3	19.4 ± 0.3	(10 min.)	44.3, 40.9, 42.7 41.6 (5.0)	(5 min.) 15.7 (15 min.) 18.5 ± 2 (2.9)
12 ppm	(x1, x3)	132.9, 59.7 (11.5)					48.4, 47.9, 47.7 48.4 (12.0)	(5 min.) 33 (15 min.) 41 ± 2 (8.5)
	(x3)	51.5 ± 1.7 (12.2)	(2000)	22.6 ± 0.2	189 ± 0.2	(5 min.)		
Air	(x3)	4.5 ± 1.5	(x500)	5 min. to -0.9 ± 0.1	0.0		10 min. to 0.5	(10 min.) 12.3 (15 min.) 8.7 ± 0.5
4.5 ppm	(x1.0)	50.0 ± 2 (4.1)	(x500)	29.1 ± 0.9	25.3 ± 0.7 (4.11)	(5 min.)	12.2, 12.3, 12.0 12.8 (3.3)	(5 min.) 12.3 (10 min.) 8.2 ± 0.5 (2.5)
Permeation Tube = 3.17 ppm			(x500)	24.0 ± 0.5	19.5 ± 0.5			

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* Calculated ppm values based on net MV, above zero blank.

** Add 10 MV (+ 0.8 ppm) to RAC, as estimated correction for improper zeroing.

of scale. The observed value for the nominal 3 ppm blend was 10% low, at 17.2. The reading for the nominal 4.5 ppm check blend was 25.3, which gives a calculated value of 4.1 based on the 3.17 permeation tube value. This checks exactly the observed value of this blend in the Barton.

The RAC likewise gave approximately the same readings for 3 ppm at 20 minutes exposure, for 6 ppm at 10 minutes, and for 12 ppm at 5 minutes. Observed values calculated for these three are 1.7, 5.0 and 12.0 ppm, and 3.3 for the 4.5 ppm check blend. A zero correction of +10 MV for improper automatic zeroing of the instrument will add about 0.8 ppm to these readings, and bring them in line with the Barton and the Bendix. The Houston Atlas (simple tape sampler) gave observed values for the same four blends of 0.5, 2.9, 8.5 and 2.5 ppm. These are all low, and probably reflect insufficient time for full equilibration in a run period of 10-15 minutes.

A similar set of data with standard deviations for each instrument during the first month on stream is shown in Table 9. In the range of 0.5 to 3 ppm, the usual standard deviation for the Barton (Cell #2) was about 0.9, the Bendix 0.1, the Houston Atlas (Model 825) and the RAC both about 2.0. The calculated values for standard deviation were usually close to 2/3 of the range of values estimated by visual inspection.

Differences in the stability of the instruments with a constant sample are shown as standard deviations in Table 10. The first four runs relate to a single blend from a cylinder originally containing 30 ppm, and the fifth is a one half blend of the same sample.

TABLE 9

LINEARITY AND PRECISION (MV AT 3, 1.5, 0.5 ppm)

Nominal Blend, in Air	Time	Barton		Bendix (photovolt at 200)			H-A		RAC		
		Scale	(Cell #2)	Scale	#1 (TS)	#2 (H_2S)	Time	Reading	Time	Reading	Δ
3 ppm	12:50-16:00	(x3)	7.5 ± 1.5*	(x500)	27.0 ± 0.3	20.5 ± 0.3	20 min.	12.0 ± 2.0 14.0 σ 2.0	(5 min.)	86 ± 3.5	11.9
	8:25-9:00 (air)	(x3)	1 ± 0.5 0.5 σ 0.9		-0.2 -0.3 σ 0.1	0.0	20 min.	-4.5 ± 1.5 3.8 σ 0.8		98 ± 1.5 97.9 σ 1.3	0
3 ppm	9:15-10:30	(x1)	15.5 ± 1.0 15.4 σ 0.8		22.9 22.6 σ 0.2	17.2 17.2 σ 0.1	20 min.	10 ± 3 9.0 σ 2.1		87.5 ± 2 87.8 σ 1.4	10.1
1.5 ppm	10:45-12:15	(x1)	7.5 ± 1.2 7.6 σ 0.6		10.3 10.2 σ 0.1	8.5 8.5 σ 0.1	10 min.	4.5 ± 2.7 4.4 σ 1.9		94.5 ± 2.5 92.8 σ 2.3	5.1
0.5 ppm	12:25-12:45	(x1)	1.6 ± 1.5 0.6 σ 1.1	(x100)	15.1 15.3 σ 0.2	13.3 13.2 σ 0.1	10 min.	0.5 ± 1.0 0.0 σ 0.7		9.55 ± 1 95.7 σ 0.7	2.2

---

* ± values are visual range by inspection, σ are calculated standard deviations.

TABLE 10

DIFFERENCES IN STABILITY (H_2S BLENDS)

	Scale + Blank		Nominal 30 ppm				Nom. 15 ppm
			Run #1	#2	#3	#4	#5
Time: Start			10:55	11:45	13:10	15:00	14:00
Finish			11:40	12:45	13:13	15:25	14:45
Reading"			10	14	48	6	10
Barton (Cell #2)							
MV	x10	(2.5)	21.1	25.2	24.7	23.7	12.1
S.D.			0.6	1.1	0.9	0.9	1.3
$\% < 1\sigma$			80	71	71	67	70
$\% < 2\sigma$			100	100	98	100	100
net			18.6	22.7	22.2	21.2	9.6
obs. ppm			16.8	20.4	20.0	19.1	8.7
S.D. ppm			0.5	1.0	0.8	0.8	1.1
Bendix	X2000	(−0.4)					
#1 MV			35.4	35.7	35.7	36.1	19.7
S.D.			0.1	0.1	0.1	0.1	0.2
#2 MV		(0.0)	35.4	35.3	35.3	35.3	21.5
S.D.			0.0	0.0	0.1	0.0	0.3
H/A	.3(100%)						
MV		(8.0)	82.7	89.6	91.0	87.2	49.8
S.D.			1.3	0.8	0.6	2.1	1.4
$\% < 1\sigma$			70	78		50	50
$\% < 2\sigma$			100	93		100	100
ppm obs.			19.8	20.4	20.8	19.8	10.4

The cylinder gas blend had lost H_2S to the level of about 20 ppm at the time of this test. Considering first the Barton, the differences in readings in the first four periods reflect slight adjustments in sample flow, to which this instrument is quite sensitive. The standard deviation of 0.6-1.3 MV averages 0.9, or 4% of the reading, which corresponds to observed values of 20.0 ± 0.8 ppm. The percent of all readings which fall within 1 σ is normal, ranging from 67 to 80, but it is unusual for 98-100% of all to fall within the 2 σ limit. This was a consistent pattern for the Barton, and it is attributed to the internal properties of the cell.

The criticality of gas flow rate control in the Barton is easily overlooked. Typical data on this effect are shown in Table 11. Deviations of ± 25 cc from the normal flow rate of 250 cc/min. give an immediate inversely proportional change of ∓ 10% in the analytical value obtained.

TABLE 11

BARTON DEVIATIONS WITH CHANGES IN GAS RATE

Air cc/min	MV Reading (x3)			H_2S, ppm	
	Zero	Reading	Net	Calc.	Equiv/250 cc
150	2.5	48	45.5	12.7	7.62
225		33	30.5	8.5	7.64
250	2.0				
275		27	25	7.0	7.69
300		25	23	6.4	7.68

In the comparative results presented in Table 10, as in Table 9, the Bendix showed much better stability for the same periods on test, ranging between 35.4 and 36.1 MV. It is relatively insensitive to changes in sample flow rate, which must be critically controlled for the Barton and other instruments. The standard deviation of readings is far superior, at 0.1 for most observations. The one half blend deviations are a little high for all instruments, suggesting that the composition of this blend was less exactly controlled.

The Houston Atlas is higher in standard deviations, from 0.6 to 2.1, and somewhat less sensitive than the Barton to changes in flow rate. The observed values which it gives are close to the Barton and follow the same pattern, allowing for the characteristic time lag of about 25 minutes (± 5 minutes) in H_2S sample readings. Tests on the RAC in other series showed a similar standard deviation range of about 1.5 to 4, and a sensitivity to changes in flow rate comparable to the Barton.

3.2.1.2 Changes in Scale

Linearity to changes in attenuation scale from x0.3 to x100 with the Barton is good, as illustrated further in Table 12. The ppm values observed for the first blend at x1, x3, x10 and x30 fall within

TABLE 12

LINEARITY TO CHANGES IN SCALE

Scale:	0.3x	x1	x3	x10	x30	x100	x3	x3 (+ fresh electrolyte)
Cell #1 **Blank (in air)**							**Cell #2**	
Start	14:07	14:36	14:54	15:09	15:23	15:40	9:55	
Finish	14:11	14:40	14:57	15:13	:27	:48	10:47	
Readings	25	25	15	26	24	51	53	
Mean MV	15.5	9.0	4.4	2.1	1.3	1.2	3.5	
S.D.	0.33	0.31	0.12	0.21	0.1	0.17	1.1	
% <1σ							66	
% <2σ							96	
Sample								
Start	14:11	14:46	15:01	15:18	15:31	15:52	11:30	13:18
Finish	14:15	14:51	15:05	15:21	:33	:54	12:20	14:17
Readings	27	29	26	15	12	12	51	60
Mean MV	>300(1)	30.3	11.8	4.5	2.1	2.0	31.4	30.3
S.D.		0.40	0.48	0.1	0.1	0.1	1.2	1.0
%<1σ							69	58
%<2σ							92	100
Net								
Reading	--	21.3	7.4	2.4	0.8	0.8	27.9	26.1
ppm obs.	>0.9	2.0	2.1	2.1	2.1	6.9	7.53	7.05
S.D. (ppm)		0.04	0.13	0.08	0.03	0.9(2)	0.32	0.27

---

(1) Off scale

(2) x100 reading is meaningless, too close to blank and SD.

the narrow range of 2.0 to 2.1 (2.02 to 2.13). The x100 reading is too low and meaningless for this sample, however, since it falls within 1 σ of the zero blank. The reading at x0.3 allowed much too short a time for equilibration, but an interval between readings of about 20 minutes was entirely adequate at the higher scale settings.

The standard deviation of readings is consistently higher for both the instrument zero and sample readings at the lower scales, as indicated above in Table 6. It also varies with the individual cell. Cell #1 operated somewhat more smoothly than Cell #2 which gave the results in Table 10 and the second half of Table 12: its standard deviations were about 0.3 (from 0.1 to 0.5) compared to 1.0 (from 0.6 to 1.3). Table 12 also shows that when readings with Cell #2 had became more erratic as the cell solution was used, they were restored to a normal range by supplying fresh electrolyte (100% within 2σ).

More complete data on linearity to scale and speed of response are given in Table 13. This is a continuous set of readings in which the scale was changed from x1 to x3 (at the end of column 1), from x3 to x10 (at the end of column 2), and so on. The "zero-time" reading in each column shows an immediate effect of the scale change, within 5-10 seconds. The response time is consistently 2 minutes or less for 98% of the final reading change on going up scale, with the zero-time effect of overshooting the final reading on each change

TABLE 13

LINEARITY AND SPEED OF RESPONSE (MV READINGS) CELL #1

Time (minutes)	x1	x3	x10	x30	x100	x30	x10	x3	x1
0	86.9	43.2	36.1	13.6	2.4	4.9	11.6	28.8	75.7
2	86.8	33.3	12.6	5.2	1.7	5.0	11.5	29.2	75.2
4	83.4	32.0	12.0	4.9	2.0	4.7	11.4	29.9	77.2
6	86.7	33.9	11.8	4.9	1.9	4.6	11.7		77.1
8	84.5	32.5	11.7	5.1	1.6	5.0	11.5		74.2
10	83.8	34.1	11.1	4.8	1.9	5.0	11.4		79.3
12	86.5	32.7	11.6		1.9	4.8	12.0		81.5
14	84.7	33.1	11.9			5.1	11.6		
16	85.1	33.7	11.5			5.0	11.2		
18	84.7	33.9	11.8			4.8	11.1		
20	84.4	34.6	12.2			5.3	11.2		
Mean	85.1	33.2	11.8	5.0	1.8	4.9	11.4	29.3	77.1
S.D.	1.26	0.73	0.40	0.16	0.15	0.20	0.25	0.56	2.5

2 minutes to 98% of scale change going up scale; overshoots at each change. Immediate to 98% of scale change going down scale, as far as 10x; slow at 3x and 1x.

Blank (air)	8.1	4.2	2.5	1.8	1.0	1.8	2.5	4.2	8.1
Net Reading	77.0	29.0	9.3	3.2	0.8	3.1	8.9	25.1	69.0
Calc. ppm	7.7	7.8	8.0	8.3	7.2	8.1	7.7	6.8	6.9
S.D. (ppm)	0.13	0.20	0.34	0.42	1.05	0.52	0.22	0.15	0.25

up-scale. The reason for this is explained in Section 3.1.1 above, and in Volume I. For each increase in scale setting there is built into the instrument an automatic increase in the rate of bromine generation, to compensate for an expected increase in demand for titration reagent at the higher range. As a result, the signal overshoots each time the scale setting is moved up, and undershoots to a slightly lesser extent each time it is moved down. The zero-time response is 98% of final reading going down scale as far as x10, but slower at x3 and x1.

The effect is not great enough to be disturbing either up-scale or down at the x1 scale or higher. This covers the range starting from 0.1 ppm, for a reading of 1 MV, or one scale division on the chart. Readings at the higher scales place a strong leverage on the blank, since the uncertainty at reading levels of 10 times the standard deviation (zero or net) equals ± 10% on the result.

The caution necessary in using attenuations below the x1 scale is illustrated in Table 14. This is a series of three blank runs and three runs on a 2.80 ppm permeation tube blend at the x0.3 scale. Starting at a previous sample reading of 88, the blank reading on air took 15 minutes to reach 90% of final response. It had not reached a final at 10.5, at the end of 4 hours. The visual range of readings at this point was ± 1.5 MV. Two blank runs starting at the other end of the scale with a zero sample reading came up to 10 and 9 in 15 minutes. These are within -1.5 MV of the 10.5 reached on coming down scale. Sample run #1 starting from a "zero" level of 11 was still climbing at 86.5 at the end of 4 hours, and run #2 reached

TABLE 14

SLOW RESPONSE ON BARTON x0.3 SCALE

(Permeation Tube: H_2S at 2.80 ppm)

Scale x0.3 Time	Blank			Run #1	Run #2	Run #3
Start	88	0	0	11	10.5	17
15 min.	17	10	9		85	
1 hr.	13			79	89	88
2 hrs.	12			83		
3 hrs.	11			85		
4 hrs.	10.5			86.5		
16 hrs.					93.5	
Visual Range	±1.5			±1	±1.2	
Sample ppm obs.					2.45	
ppm (perm. tube)					2.80	

Start-up Equilibration Time on x0.3 Scale = >15 min.
(from 0.0 to blank for air) x1 Scale = 1 min.
x3 Scale = <1 min.

93.5 in 16 hours, overnight. Run #3 gave about the same reading as Run #2 at the end of one hour, but starting from a much higher "zero". The 93.5 MV reached at the end of 16 hours corresponds to an observed value of 2.45 ppm on the 2.80 ppm sample.

The reproducibility between any of these readings short of equilibrium is not reliable. The Barton handbook recommends dumping the inner cell electrolyte by hand each time the scale is changed, at attenuations of x0.1 or x0.3. Even this is not enough to correct the very slow response to changes in sample, or changes from sample to blank to sample, at a constant low scale setting. This very slow equilibration is apparently related to the circulation of electrolyte between the inner and outer cell chambers. It should be greatly improved by better circulation.

Linearity to concentration in the Bendix is affected to some extent by increases in photomultiplier voltage which expand the scale. Data for low concentration blends at three settings are shown in Table 15, for both the TS and H_2S channels of the instrument. The increase is directionally higher at the lower concentrations. This is in line with the observation that the more expanded scales tend to become non-linear at a lower concentration, which was found in the more detailed data presented below for COS (Figure 16).

3.2.1.3 Tests for Accuracy

Most of the data obtained in this program, like those in Tables 6 to 15, were tests on operability and precision, not accuracy. Tests for accuracy require a known sample with an instrument of

TABLE 15

BENDIX PHOTOMULTIPLIER EFFECTS (TS/H_2S)

ppm H_2S (Nominal)	Attenuation Scale	TS/H_2S Readings, MV at Photomultiplier Settings:			Ratios of TS/H_2S Readings at Different Settings	
		200	50	0	200:50	200:0
3	x500	23.4/17.3	14.4/10.5	12.2/8.8	1.63/1.64	1.92/1.96
1.5	x500	11.0/8.9	6.6/5.1	5.5/4.1	1.67/1.74	2.00/2.17
0.5	x500	3.1/2.5			x100: x500	
	x100	16.0/13.2			5.16/5.28	

constant calibration, under fixed operating conditions. This combination was rare and such tests were run on a relatively few occasions, since the project involved a continuing series of changes to achieve operability with instruments not originally designed for the stack gas range. This was particularly true for the Bendix where repeated changes were made in GC packing, gating, photomultiplier voltage range, automatic zero imbalance and combinations thereof, and each required essentially a new calibration. Tests for accuracy against permeation tube blends were therefore run (primarily) on the Barton, which had its own calibration curves, and less often on the Houston Atlas and RAC.

Accuracies of about + 2% above calibration are shown in Table 16 for Barton Cell #1 and + 6% for Cell #2, at known concentrations of 4.36 and 9.17 ppm of H_2S. A cylinder blend to match the lower known sample was made, and a calculated higher blend derived from this by volumetric proportion. The second blend, run overnight, gave a completely different value from its daytime setting. Investigation revealed that this blend was prepared from a Teflon lined cylinder, which released more H_2S when cool at night than when warm during the day. The ratio was 7.8 to 6.2 at a constant dilution, or 16.6 to 13.2 at a higher flow rate.

Cell #2 in these permeation tube tests shows the same higher standard deviation as before, but Cell #1 had deteriorated slightly,

TABLE 16

TESTS FOR ACCURACY

(Permeation Tube: H_2S)

	Barton (Cell #1)				Houston Atlas		Barton (Cell #2)		
	Cyl.	Perm.	Perm.	Cyl.	Perm.	Perm.	8 ppm	9.1 ppm	4.3 ppm
Blend: Start	13:35		16:20				13:40	13:05	11:15
Finish	14:15		16:20				17:30	14:45	11:30
Readings	10		2				11	11	3
Mean	5.1		6.2				4.5	7.5	
S.D.	0.2		0.1						
	4-28	42-49	55-58	76-49	42-49				
Sample: Start	11:20	14:30	15:35	18:20	14:30	15:15			
Finish	13:25	15:05	15:50	8:40*	15:05	15:25			
Readings	26	8	3	44	8	3			
Mean	20.1	20.5	39.6	29.3	30.6	43.8	36.3	42.8	23.9
S.D.	0.5	0.9	0.2	0.5	7.0	3.0	1.3	1.5	0.6
% <1σ	77	75		77	62	67	73	63	67
% <2σ	92	100	100	98	100	100	100	100	100
ppm obs.	4.20	4.32	9.35	6.46	7.14	10.5	8.9	9.89	4.59
ppm calc.	(4.31)	4.36	9.17	(5.14)*	4.36	9.17		9.17	4.36
% Error obs.		-0.9	+2.0		+64	+15		+7.8	5.3

---

* H_2S concentrations in Teflon-lined cylinder-blend changes with temperature: daytime 6.2 ppm to night 7.8 to day 6.2; at different flow rate day 13.2 to night 16.6.

after 4 months in use, and is averaging about 0.5 (0.2 to 0.9) as compared to its initial averages of about 0.3. This is attributed to slight differences created in cleaning the cells, during prolonged experimental use.

Houston Atlas tests on the same samples showed high results and high standard deviations, approaching 25% of the mean observed. This is higher than usual for the instrument, but not predictable, since it depends in part on unevenesses in the paper tape.

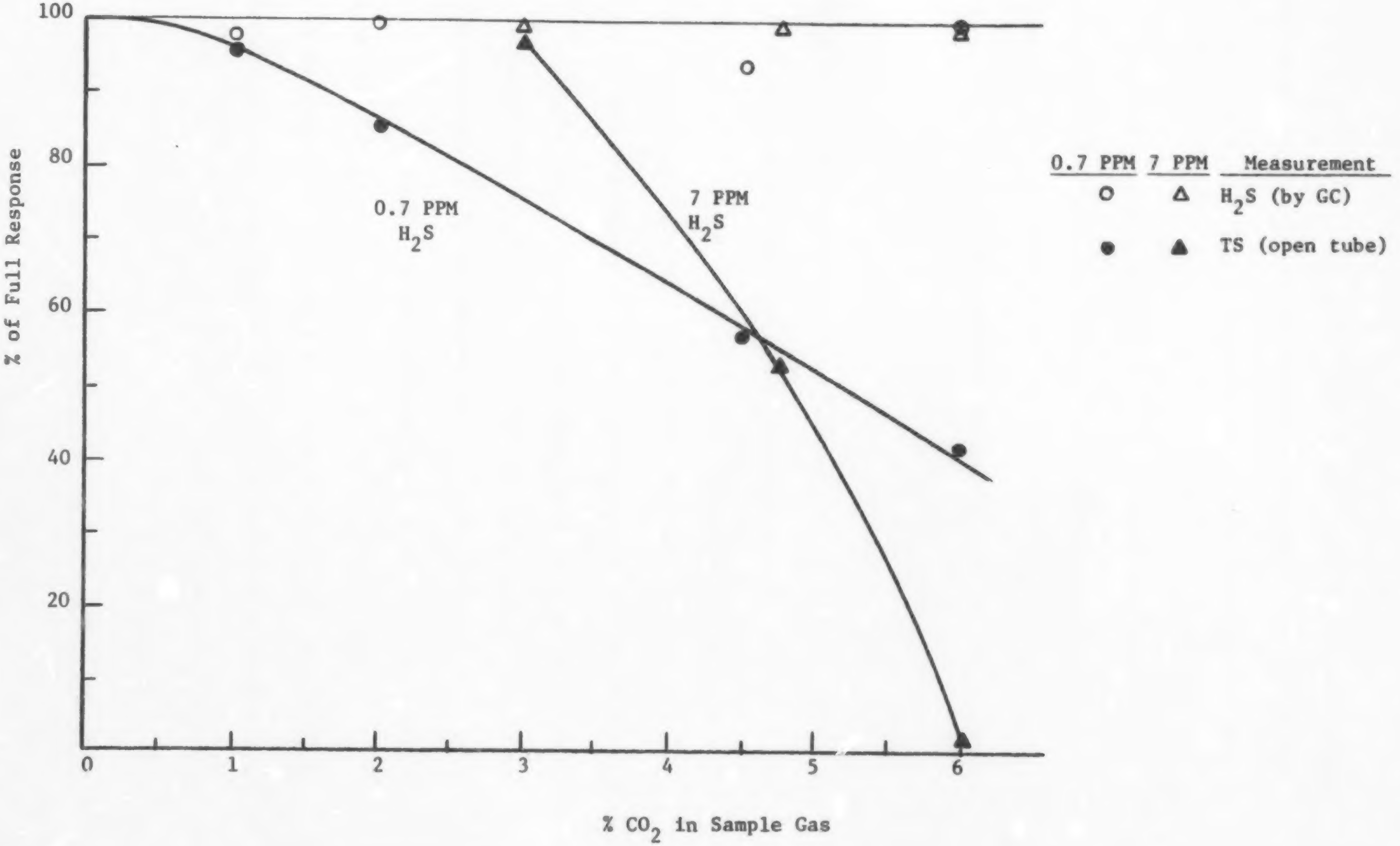
3.2.1.4 Effect of Stack Gas CO/CO_2

The interferent effect of stack gases on analytical results reflects their composition and also the very large or overwhelming ratio they may have compared to the odorant gases to be measured. This has been noted above with respect to water, and with the FPD sensor it applies to both CO and CO_2. Percentage amounts of either gas in a combustion stack will completely mask the FPD response to S compounds at 0-10 ppm. Data on this effect are given in Figure 15. The same result appears in blends containing hydrocarbons at percentage levels or higher. These ratios do not usually occur in combustion stacks, but they can occur in other vented gases.

The amount of CO_2 it takes to suppress the FPD response is roughly 4000 times the amount of S present. Less than 3% of CO_2 has no effect on the response to an H_2S blend of 7 ppm, but amounts above 0.5% begin to show the effect with an H_2S blend of 0.7 ppm. At this ratio the background or noise level due to CO_2 becomes equal to the

FIGURE 15

EFFECT OF CO_2 ON BENDIX
RESPONSE (PPE, x100) AT DIFFERENT S LEVELS



signal, even though it can be ignored when the interferent and S compound are present at an equal order of magnitude. Qualitative tests showed an equivalent effect for CO, CO_2 and butane in air, without the GC column.

This interference has no effect on the Bendix response in Channels 2 and 3 of the instrument as supplied. These use the GC/FPD combination to measure H_2S and SO_2. It destroys the response to total S in stack gases in Channel 1, which measures the signal from a portion of the untreated original sample. This places an important constraint on the choice of GC packings which can used to obtain special separations. They must be able to separate CO, CO_2 and hydrocarbons if present, from the S compounds to be measured. This is true for polyphenyl ether/H_3PO_4 on Teflon as supplied with the instrument, but there are many other packings to which it does not apply.

A brief review of scrubbing procedures as a possible alternate to GC separation indicated considerable difficulties in obtaining a satisfactory separation of CO_2 from SO_2 and H_2S, and even less promise for a quantitative separation of CO.

3.2.2 Interference from SO_2

3.2.2.1 Effect on H_2S Response

SO_2 is not distinguished from H_2S in the Barton and gives an additive response when both are present, as indicated above. The conversion factor for SO_2 is 2.3 times that of H_2S (Table 5), so a small scale reading represents a relatively large amount of SO_2. The Bendix separates the two by GC and gives entirely independent measurements. The simple Houston Atlas (Model 825) and RAC recorders have a low tolerance for SO_2, which bleaches the PbS color on the tape. Data showing these effects are given in Table 17.

The Barton values for concentration are taken as a reference point, starting with an air blank on all instruments. The first sample was 10 ppm of H_2S and SO_2 was added to this in three successive increments. Results on the Bendix for H_2S alone and the first increment of 45 ppm of SO_2 are exactly additive for total S, as the sum of H_2S and SO_2. This amount of SO_2 diminishes but does not totally suppress the initial response of the two tape recorders to H_2S, and has about the same effect on both instruments. A larger increment of SO_2 to 130 ppm is nearly but not quite off scale for the Bendix, at 29.5 MV for SO_2 vs 30.9 for total S. This amount returns the Houston Atlas reading to its zero level, but still leaves a detectable small response for the RAC. Continued exposure at a slightly higher SO_2 level of 150 ppm is off scale for the Bendix and gives no response for the RAC. At both the 130 and 150 ppm levels the response of Bendix Channel #2 to H_2S is unaffected, even though both Channels #1 for TS and #3 for SO_2 are going off scale. The upper response limit of 130-150 ppm shown here for SO_2 checks the 120 ppm limit for H_2S discussed earlier in Figures 3 and 4. The MV level of the limit (and readings) is different, because these data were obtained at a photomultiplier setting of 50 instead of the usual 100. The response limit is the same for separations using the PPE packing (Table 17) and Poropak Q (Table 3), since it depends only on the gas analyzed and not its method of separation.

TABLE 17

EFFECT OF SO_2 ON H_2S RESPONSE

Scale	Barton		H-A	RAC	TS Bx #1	H_2S Bx #2	SO_2 Bx #3	ppm Calculated			Bx Response
	x3	x10	F.S.	5 min.	x2000 (50 photo)			Ba	H-A	RAC	
Zero	3.5	3.0	7	-.8	-.3	0	0				
H_2S ($\sim$10 ppm)	38.7		37	-37.4	9.6	9.8	-.1	9.9	7.5	6	#1 = 2 + 3
$+SO_2$ ($\sim$45 ppm)		24.0	20	-13.0	27.4	9.8	18.3	(+20)	3.2	2.5	#1 = 2 + 3
$+SO_2$ ($\sim$130 ppm)		78.5	7	-3.1	30.9	9.9	29.5	(+129)	0	0.5	End of Scale
$+SO_2$ ($\sim$150 ppm)	280	100.1	7	-.8	31.2	10.0	31.1	(+150, 172)	0	0	Off Scale

Conclusions: Bx is almost off scale at 129 ppm.
Bx H_2S is not affected, as SO_2 and TS go off scale.

TABLE 18

EFFECT OF SO_2 CYCLES ON H_2S RESPONSE

Gas Conc.	Bendix (x1000) #2 (H_2S)	Bendix (x1000) #3 (SO_2)	RAC MV	RAC (ppm)	Houston Atlas MV	Houston Atlas (ppm)
Air (blank)	1.1	0.9	-1.0			
H_2S (3.5 ppm)*	26.7*	0.8	26.1* (1.7)	(4)	31 ± 9	(7.7)
(8.0 ppm)	58.8	0.7	54.6	(11)	44 ± 3	(11)
(3.5 ppm)*	26.7*	0.7	23.7*	(3.7)		
H_2S (3.5) + SO_2 (15)*	25.5*	57.0	13.9-6.5	(2 - 1)		
H_2S ($\sim$6 ppm)	45.0	0.7	51.8	(10)		
+ SO_2 (15)	45.3	82.6	23.9-7.6	(3.7-1.2)		
+ SO_2 (Scrubbed, old soln.)	40.2	6.1-24.9	21.7-15.6	(3.5-2.5)		

---

* Check runs

A second set of data showing the effect of several cycles of increasing and decreasing concentration is shown in Table 18. Check runs on H_2S of the same concentration with or without added SO_2 gave check results in Bendix #2, within the accuracy of the sample. Check results with the RAC were less precise for H_2S alone,and the addition of SO_2 caused an immediate loss in response, with a further loss in the next 5 minute cycle. The addition of a Barton SO_2 scrubber partly restored the RAC response, at first, but this scrubber contained a used solution. This was soon exhausted, and as the SO_2 response in the "scrubbed gas" went up in Bendix #3, the RAC response went down.

The Houston Atlas Model 855 which is not shown in these data converts all SO_2 and other S compounds to H_2S, and makes no distinction between them. The chief problem in this instrument was the time lag of about 25 minutes with all compounds, due to mixing effects in the conversion chambers and unheated lines. This lag was as much as an hour for samples containing moist SO_2, or some of the heavier S compounds. When the concentration of sample containing one of these gases was dropped there was a fairly prompt partial drop in reading, but a long equilibration time to show the full effect. This behavior may be attributed in part to line adsorption and desorption inside the instrument.

3.2.2.2 KAP Scrubber for SO_2 Removal

The potassium acid phthalate (KAP) scrubber for SO_2 removal supplied as part of the Barton system uses a solution containing 30 g. of KAP per quart, or 0.155 mols per liter. The theoretical absorption capacity of this scrubber is 10 g. of SO_2 per liter of solution, assuming a molar reaction. This is equivalent to 10^6 liters of gas at 3.74 ppm (at 20°C.). At the normal Barton gas feed rate of 250 cc/minute, this corresponds to 24 hours of gas flow at 10,390 ppm. This would represent a maximum useful life of 1000 days at 10 ppm of SO_2, in the ambient range, but only one day or less at an average stack gas SO_2 concentration of 1% or more.

The selectivity of the KAP solution for passing H_2S while retaining SO_2 varies with the concentration. It is reported as a 10-15% loss of H_2S at the 1 ppm level and a tenth of this at the 20 ppm level, in tests by Blosser and Cooper using a continuous flow of fresh solution (5). Data obtained in the present program confirm the loss of 10-15% on scrubbing at low concentrations, in the range of 0-10 ppm. A typical result is the last entry in Table 18, which shows 12% of the H_2S lost on scrubbing (a decrease from 45.3 to 40.2 MV in Channel #2), with a feed gas containing 6 ppm of H_2S and 15 ppm of SO_2. These data were obtained with a scrubber approaching exhaustion: similar results with a fresh solution are shown in Table 19. The H_2S blends in this case were permeation tube samples having a calculated concentration of 9.17 and 4.36 ppm, and the observed Barton values represent a loss of 17-18% of H_2S on scrubbing.

Parallel tests between the Bendix and Barton did not confirm literature indications that the KAP scrubber quantitatively removes SO_2,

TABLE 19

EFFECT OF FRESH SOLUTION IN KAP SCRUBBER

	Scrubber	Barton MV (x3)		Minutes to Read		Sample by Perm. Tube	
(ppm) in Air	Action	Initial	Equil. Value	90%	F.S.	Calc.	Obs.
Air	-	-	3.5	2	5		
Air	+ (old)	11.1					
SO_2 (16)	+ (old)	11.6	26.9	30	40		
SO_2 (16)	-	91.8			5		
Air	-	6.4		4			
SO_2 (16)	+ (old)	26.6	26.0				
SO_2 (16)	+ (new)	4.1	3.7	1	5		
SO_2 (16), H_2S (9)	+	129.8	31.2	5	10	9.17	7.62(83%)
SO_2 (8), H_2S (4)	+	17.3	16.2	5	10	4.36	3.56(82%)
Same	-	64.0	64.0		5		
Same	+	13.8	16.0				
(+ 1 hr)			16.2 (σ 0.9)				
(3-5 hrs)			16.5 (σ 0.3)				
(5-13 hrs)			16.5 (σ 0.4)				
(13-15 hrs)			16.3 (σ 0.4)				

"Old" scrubber gives false high value, but reproducible after equilibration. Value comes down with new solution, reproducible at lower level. H_2S is partially absorbed (17-18%) at this level.

while retaining a constant small volume of H_2S which shows only at low concentrations. On the contrary, there is evidence that under the conditions used here, the KAP solution passes some SO_2 while retaining some H_2S; the two amounts are in approximate balance, so as to give an approximately correct reading in the Barton which does not distinguish between them. Data on this effect are presented in Table 20, taken from the "daily print-out" reproduced in Figure 5. The Barton and Bendix in this study were run in parallel, and the KAP scrubber when used was placed in line with the gas manifold, feeding both instruments. The addition of 16 ppm of SO_2 to 4.5 ppm of H_2S shows separately in the Bendix, and increases the Barton total response from 24 to 49 MV (including the zero blank), without the scrubber. Placing the scrubber in line decreases the SO_2 reading from 98 to 14 (Bx #3) and the Barton total to 18. Only on shutting off the SO_2 does Bx #3 drop to zero, and the Barton TS to 15. These data show consistently 15% of the SO_2 as unabsorbed. The action toward H_2S is erratic, depending apparently on the past history of the scrubber.

The time required for equilibration after placing the 1-liter scrubber in line is basically related to the time required for gas mixing, as discussed above with respect to the Barton surge chamber (see 3.1.1). The effect is illustrated in Table 21:

TABLE 20

KAP SCRUBBER: COMPENSATING EFFECTS BENDIX/BARTON READINGS FOR $H_2S/COS/SO_2$ (1)

Gas Blend Nominal ppm in Air	KAP Scrubber	Bendix MV (x100) #1 (H_2S)	Bendix MV (x100) #2 (COS)	Bendix MV (x100) #3 (SO_2)	Barton MV (x3)	Comments
Air blank	-	.1	-.1	-.2	7	
H_2S (2.5)	-	33.5	0	0	-	
$H_2S + SO_2$ (16)	-	33.5	0	99.5	25	
H_2S (4.5) + SO_2	-	57.7	0	98	49	
H_2S (4.5) + SO_2	+	50.8	0	14	18	Scrubber left 15% of SO_2 (Bx)
H_2S (4.5) only	+	52.5	0	0	15	Scrubber left 16% of SO_2 (Ba)
H_2S (4.5) only	-	52	0	0	24	SO_2 (Ba) reading restored
Air	-	0	-.2	-.4	8	
H_2S (4.5)	-	52	0	0	24	Check readings
$H_2S + SO_2$ (9)	-	50	0	46.5	39	
$H_2S + SO_2$ (9)	+	53	0	6.5	22	Scrubbing left 15% of SO_2 (Bx)
$H_2S + SO_2$ (9)	-	53	0	47.5	38	Check readings
$H_2S + SO_2$ + COS (30)	-	54	77	52.5	44	Initial ΔSO_2, Bx and Ba
$H_2S + SO_2$ + COS (30)	+	51	65	9	24	-20% COS, partial SO_2
$H_2S + SO_2$ only	+	54	0	7	23	More SO_2 removed
COS (30) only	-	0	103	0	14	Ba reading is false
H_2S (4.5) only	+	51 → 47	-.1	-.6	22 → 7	Ba reaches "zero" in 3 hrs
H_2S, overnight	+	47	-.4	-.7	3	Ba cell poisoned

---

(1) COS blends contain CS_2, 10/1 ratio of COS/CS_2.

TABLE 21

RESPONSE TIME WITH SO_2 SCRUBBER IN LINE (BARTON, X 3 SCALE)

Sample ppm	Initial Response Time, % of Final	Full Response Time to ± 2% of Final
Air (after high conc.)		15 min.
12 H_2S, 24 SO_2	5 min, 60%	10-15 min, 98%
7.3 H_2S	2 min, 75%	10 min, 98%
3.6 H_2S	2 min, 85%	10 min, 99%
Air (after low conc.)	2 min, 95%	5 min, 99%

The time delay of response approaches 15 minutes at anything other than low concentrations. This curve has a significant result in the automatic time cycle built into the Barton instrument for plant operation, which cuts the KAP scrubber out of the line for 10 minutes out of every 2 hours. This reads "reduced sulfur, as H_2S" for 110 out of the 120 minutes, but the 10 minutes off scrubbing is less time than is required for full equilibration of the response. Thus, the answer which this provides for "SO_2 by difference" is an empirical reading which may be correlated with plant operation, but it is not an absolute value. To be realistic, not much more would be gained in accuracy by allowing more equilibration time, since the final correlations with plant operation will still be empirical. If more information is desired on actual measurements of SO_2 and H_2S or other components, a GC separation is much to be preferred.

3.2.3 Effects of Carbonyl Sulfide

3.2.3.1 Response and Interferences

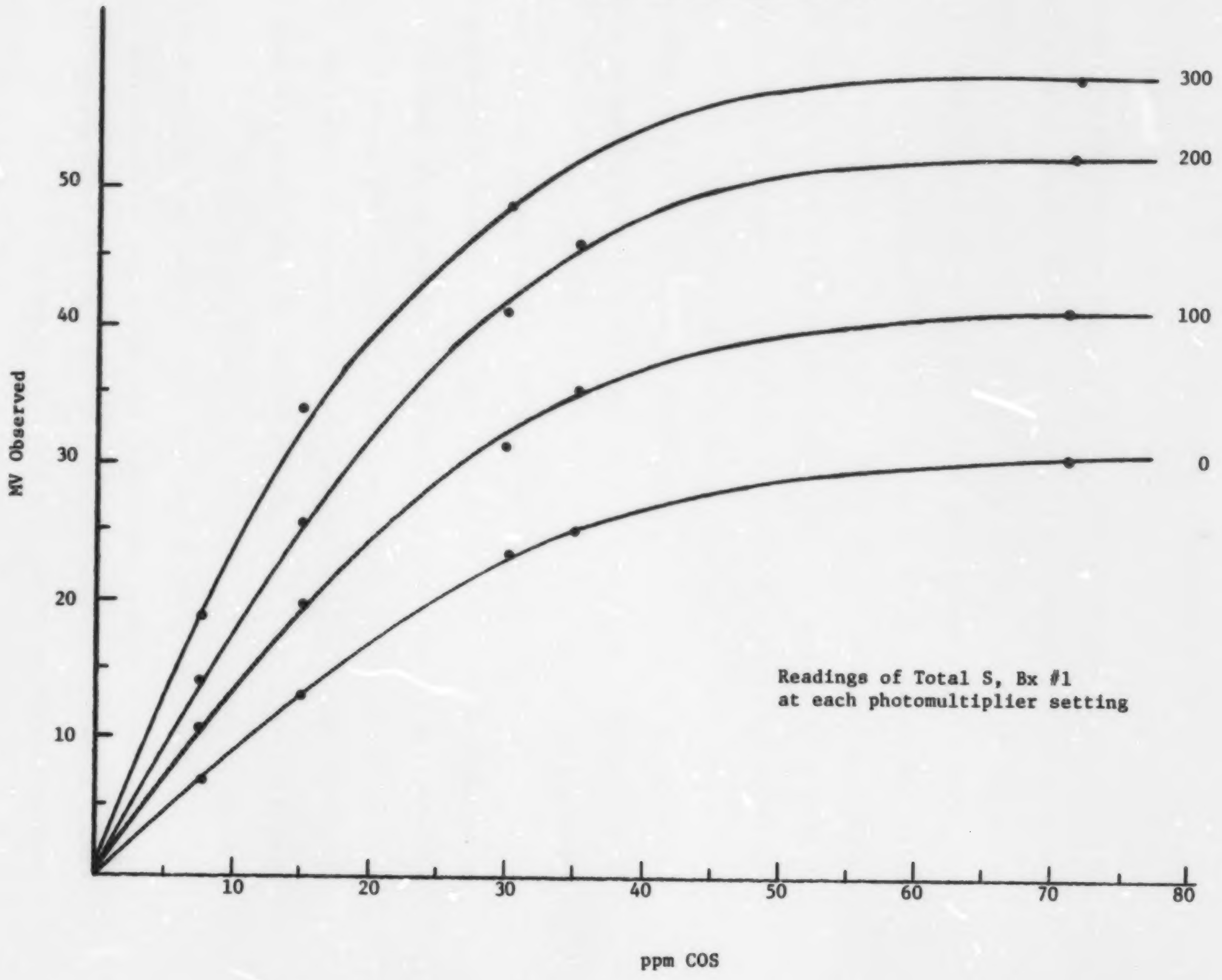
The original assumptions made as to the effect of COS on the detection and measurement of other sulfur-containing gases changed significantly during the course of this study. The initial picture was that the Barton and RAC do not respond, while the Bendix and Houston Atlas (catalytic unit) give a full response. The first complication is that COS itself is slowly hydrolyzed to H_2S in moist air. This is a probable contributing factor to conflicting reports in the literature on the odor of COS, which is usually reported as odorless. The Barton is very sensitive to H_2S, and a standard gas cylinder blend of COS which gave no response at the 250 ppm level at the start of this program gave a response 10 months later equivalent to 0.2 ppm of H_2S. This could be due to either a 0.1% hydrolysis in the cyclinder, or a more critical evaluation of the data based on longer experience.

The response of the Bendix to COS is quantitative and equal to H_2S on an equal volume (mole) basis, but only at low to moderate concentrations. A calibration curve showing the linearity of response in the range of 0-35 ppm and the effect of photomultiplier voltage setting is shown in Figure 16. These data were obtained with the original GC packing of polyphenyl ether (PPE) plus H_3PO_4, on Teflon. The gas blends were made up from COS in air.

Linearity to COS is somewhat better at the lower voltage settings of the photomultiplier potentiometer, although higher settings spread the scale. Linearity is almost identical at the 0 and 100 settings, and the standard setting at 100 was selected on this basis.

FIGURE 16

BENDIX LINEARITY TO COS, 0-35 PPM



The deviation of individual Bendix COS readings from the smoothed curve is about ± 0.5 ppm, up to 35 ppm. A straight line calibration is within ± 2% of the readings up to 20 ppm, and another straight line of different slope can extend this range to about 40 ppm. These data indicate that the upper limit of linearity in the FPD sensor is lower for COS than it is for H_2S and SO_2 (Figures 3 and 4). This relationship merits further research, which is beyond the scope of the present project. It is presumably tied to the chemistry of COS in the hydrogen-rich flame.

A complicating factor in the study of COS in the Barton, with or without the scrubber, is the unusual behavior of the Barton cell on exposure to carbon disulfide. The incorrect assumption was made at the start of the program that the Barton does not respond significantly either to COS or to CS_2, which is present regularly in small amounts in field samples containing COS. The standard cylinder for representative synthetic gas blends was made up accordingly, to contain 250 ppm of COS and 25 ppm of CS_2. Subsequent data indicate that the Barton does respond to CS_2, but slowly and in an anomalous manner which is not fully understood.

CS_2 in air at or below 1 ppm shows no response in the Barton cell during an exposure of 100 minutes (see Table 22, below). The effects observed here might not be noted, therefore, in calibration tests or measurements at ambient levels. A higher concentration blend at 80 ppm does respond, but only to the extent of a 3.5 MV increase in reading at the end of 20 minutes. This reading, on the x3 scale, would correspond to 1 ppm of H_2S. A shot of the straight calibration gas at 250 ppm of CS_2 (+ 2500 ppm of COS) gave a reading which continually increased, with no indication of a definite level of response. More significantly, however, the CS_2 reading does not revert to zero when the sample gas is replaced by air. Several hours or more on air are required to re-establish a blank reading, depending apparently on the cumulative exposure to CS_2 (at 80 ppm). These observations suggest that CS_2 may form some sort of molecular complex with free bromine instead of being oxidized in the coulometric titration. The net effect is to poison the cell.

A still further indication is that the KAP scrubber may convert COS in part to H_2S and in part to CS_2. The loss in activity which is discussed below for a 10:1 blend of COS/CS_2 is apparently more rapid than that obtained with the same small amount of CS_2 alone. This is a complex interaction which invites further research. The Barton, with or without its scrubber, is of no value in the measurement of COS, and it is poisoned by $COS + CS_2$.

3.2.3.2 Effects of KAP Scrubber

Comparative data for COS/H_2S blends in four instruments are given in Table 22, showing the effect of the Barton KAP scrubber on readings for TS, H_2S and SO_2. The feed concentrations given are nominal ppm in air, calculated from cylinder gas calibrations. The addition of 8 ppm or 6 ppm of COS blend to 4 ppm of H_2S shows no response or change in the Barton. The Bendix shows full response in both TS (Channel 1) and "H_2S" (Channel 2), in direct proportion to the total of H_2S plus COS. The RAC shows no change, and the Houston Atlas is qualitatively proportional to total concentration.

TABLE 22

EFFECT OF COS IN USED KAP SCRUBBER

Time	Gas Feed (ppm) in Air	Scrubber		Barton (x3)			Bendix (x1000)			RAC	H-A
		Ba	Bx +RAC	Obs.	Net	ppm	#1	#2	#3	10 Min, 40%	Range
9:45-10:20	H_2S (4)	-	-	18.2	14.1	3.8	20.7	26.5	0.3	31	33-39
-11:10	H_2S (4), COS (8)	-	-	18.2			60.0	59.3	2.0	27-33	80-90
-12:00	H_2S (4), COS (6)	-	-	18.3			50.2	50.7	0.3	29-30	58-62
-12:30	Same	+	+	87.5-39							
-13:15				36-23.4			39.0	38.0	0.4	22-32	75-82
-15:00	H_2S (4), COS (8)	-	+	18.8-8.6,9.8			51.6	47.5	0.4		67-93
				Cell #2							
-15:30	Same	-	+	22.7-21.2			48.5	43.1	0.4	35-39	77-87
-15:55	Same	+	+	35.2-33.8			49.0	44.0	0.4	35-39	75-94
-16:10	Same	-	-	23			55.9	49.6	0.4		74-97

COS/CS_2 blend causes sharp increase in Ba, then loss in activity.
New Ba cell shows activity restored, but pattern is repeated.

The COS blends in this series were all made up from a cylinder containing 250 ppm of COS plus 25 ppm of CS_2, so that "8 ppm" of COS actually means 8 ppm of COS and 0.8 ppm of CS_2. The Barton showed no response to either constituent during 100 minutes, without the scrubber. This was considered at the time as evidence that the Barton does not respond to CS_2, as well as COS, and tests were continued using the calibration blend.

The KAP scrubber caused an immediate drop in Bendix TS and H_2S (after time 12:00, Table 22) and an immediate increase in these readings when it was subsequently removed (after time 15:55). The Barton, on the contrary, showed a sharp increase on scrubbing, to over twice its previous reading (time 12:00 to 12:30). This can only be interpreted as converting a material inert to the Barton (COS) to an active form, or stripping out of the scrubber materials previously retained (SO_2 or CS_2), or both. On further scrubbing, the Barton value fell and continued to decrease for another hour.

Two separate KAP scrubbers were employed for these tests, one for the Barton and the other for the Bendix and RAC, to avoid overloading the scrubbing action by a high gas rate. At this point the Barton scrubber was taken off line (13:15), but the Barton reading continued to decrease even without the scrubber. It was apparent that something in the COS/KAP combination had poisoned the cell (#1), and it was switched to a new cell (#2) with fresh electrolyte. The reading was restored promptly to 21 MV for cell #2 (vs. 18 MV for cell #1), without scrubbing. The Bendix at the same time (15:00 to 15:30), on the same gas stream as the Barton, but with continued scrubbing, showed a 20% increase in TS and H_2S, corresponding to a 20% increase in the total of H_2S (4 ppm) plus COS blend (6 ppm to 8 ppm).

The same pattern was repeated with the new Barton cell and fresh electrolyte. Placing the KAP scrubber in line caused an immediate increase on the Barton from 21 MV to 35, and this fell off gradually to 33 in 25 minutes (to 15:55). At this time both KAP scrubbers were taken out: the Barton reading dropped promptly to 23, and the Bendix rose to 56/50 on the first cycle.

The RAC was running on the same gas stream and scrubber as the Bendix during these changes. Scrubbing caused an initial slight drop in reading, which was not clearly outside the experimental error. Continued scrubbing showed directionally a slight increase in reading. This suggested that some of the increase in Barton might be due to COS absorbed in the scrubber and converted to H_2S. The Bendix with PPE packing can not answer this question, however, since it is equally sensitive to H_2S and COS in both channels #1 and #2. The Houston Atlas, with no scrubbing, showed the expected response to total concentrations of 4, 10 and 12 ppm but its deviations between readings are as great as the difference in response between the 10 and 12 ppm samples.

The possibility that the COS blend was stripping something out of a "used" KAP scrubber solution was considered next, in the tests shown in Table 23. The same pattern of Barton and Bendix results as before was obtained on adding 8 ppm of COS blend to 4 ppm of H_2S, without, with, and without the KAP scrubber. The used KAP solution in both scrubbers was then replaced with fresh KAP. The Bendix showed the same results (COS absorbed) with fresh solution, but the Barton showed no corresponding increase.

TABLE 23

COS + SO_2 IN KAP SCRUBBER

Scrubber	Gas	Barton (x3) (Cell #2)		Bendix			RAC Range
		MV	ppm	#1 (TS)	#2 (H_2S)	#3 (SO_2)	
-	Air	5.0					
	H_2S (4 ppm)	23.0	4.7	9	22.7	0.4	29.3 - 32.0
-	H_2S + COS (8 ppm)	23.0	4.7	57.1	52.7	0.4	(37.2) 30.5 - 28.7
+ (used)	H_2S + COS	33.8	7.8	48.1	43.7	0.4	22.5 - 30.2
-	H_2S + COS	23.5	4.8	56.5	51.2	0.4	31.6 - 28.5
+ (new)	H_2S + COS	23.0	4.7	51.0	45.7	2.8	26.3 - 25.5
-	H_2S + COS	23.0	4.7	55.4	51.1	0.4	23.4 - 28.6
-	H_2S + COS + SO_2	46.8	14.8 $(\overset{obs.}{SO_2})$	101.2	51.0	55.8	18.8 - 12.9
+	H_2S + COS + SO_2	23.5	(=initial, no SO_2)				
	(10 min.)			46.0	39.5	3.9	
	(30 min.)	26.8		50.5	42.4	7.1	
	(2 hr.)	28.1		52.4	41.4	15.0	
	(4 hr.)	31.7		56.5	43.7	19.6	
	(8 hr.)	32.7		58.5	44.1	21.4	
	(13 hr.)	36.1		65.9	45.0	23.6	

This suggested that the gain in Barton reading was due to a reaction with or displacement of the SO_2 absorbed in previous use. This theory was tested by adding 14 ppm of SO_2 to the H_2S/COS blend, with fresh KAP in both scrubbers. The SO_2 increment in the Barton readings was quantitatively removed at first but the scrubber began to fail at once, with both SO_2 and COS present. The readings continuously increased with continued exposure. The Bendix reading for H_2S (from COS plus H_2S) was unchanged by the added SO_2 before scrubbing, but it came down to a lower level on scrubbing than it did on scrubbing without the added SO_2. In other words, the interaction of SO_2, COS and KAP definitely caused more absorption of COS than with the COS blend and KAP alone. The presence of CS_2 has no effect on this comparison, since it is separated in the Bendix GC and does not come out with H_2S.

On continued exposure overnight, the Bendix channel 3 results (Table 23) indicate an increasing release of SO_2 through the scrubber, and an apparent gradual increase in readings for H_2S. The KAP scrubber by this time has almost completely failed, and all readings, both Barton and Bendix, have regained 40 to 50% of the initial decrease or increase observed on scrubbing. The RAC showed no response to this COS blend, with or without scrubbing, but lost half its reading for H_2S on adding SO_2 to the sample.

The Bendix #3 readings for SO_2 in Tables 22 and 23 are not adequately explained. The addition of COS apparently released SO_2 on two occasions, both of which may be due to an initial purging of adsorbed gas on first introducing the COS blend (SO_2-free) to a gas manifold or scrubber which has had previous contact with SO_2. The effect was erratic, if real, and it is not known whether this was due to COS itself or possibly to the effects of CS_2 in the blend. The tests on CS_2 alone discussed above (Section 3.2.3.1) were run at the end of the project, and it is obvious that the definition of its effects requires further research.

A continuous KAP scrubber of reduced gas hold-up was recommended by Blosser and Cooper (5). This would also have the advantage of avoiding continued contact with spent solution. The time factor of gradual failure noted in Table 23 above directed attention to continuous scrubbing as a possible improvement. Tests were conducted in a column made up from a 3 foot section of 1 inch tubing packed with irregular 1/2 x 3/4 inch glass cylinders. This had a 100 cc of liquid hold-up at a liquid flow rate of 180 cc/hr. The results obtained are shown in Table 25. The concentrations given are nominal values, for synthetic gas blends. At a gas rate of 1 liter per minute, SO_2 was completely removed at 200 ppm in air, but only partially removed at 400 ppm or more.

The addition of 15 ppm of COS blend (1.5 ppm of CS_2) caused a marked increase in Bendix SO_2 and Barton total S. The poisoning effect of the COS/CS_2 was decreased by the addition of 6 ppm of H_2S, but not eliminated since neither the Barton nor Bendix response is normal for this amount of H_2S. A slight increase in SO_2 content from 200 to 280 ppm shows that the COS blend has greatly decreased the capacity of the scrubber for SO_2 removal. Another increase in H_2S to 10 ppm directionally reduces the poisoning effect of the COS blend, but neither the Barton nor Bendix readings are normal. Continuous scrubbing did not cure the problems of the KAP reaction, and the results obtained can only be interpreted by further research.

TABLE 25

CONTINUOUS FLOW KAP SCRUBBER

180 cc/hr., 100 cc on wetted column
1 ℓ/min. total gas flow

Gas Blends Nominal ppm in Air	Response ppm				Comments
	Barton		Bendix		
	as H_2S	as SO_2	TS	SO_2	
SO_2 (700)		8	10	8	Partial removal
(500)		4.5	7	5	
(400)		3	5	4	
(200)		0	0	0	Limit of complete removal
SO_2 (200) + COS (15)	3		15	29	COS releases SO_2
SO_2, COS + H_2S (6)	5	-	9	15	H_2S reduces effect of COS, less SO_2 released
SO_2 (280), COS (15), H_2S (6)	(6)	+17		16	COS decreases capacity for SO_2 removal
SO_2 (280), COS (15), H_2S (10)	(10)	+16		10	H_2S reduces effect of COS

3.2.3.3 Alternate GC Packings

The failure of the Barton cell in samples containing COS/CS_2, with or without the KAP scrubber, rules out this instrument for use in refinery stacks such as the Claus plant burner, cat cracking regenerator, or fluid coke burner. The failure of the KAP scrubber in gas streams containing both SO_2 and COS likewise rules out its use to achieve operability for the RAC tape recorder, or to distinguish between total sulfur and total reduced sulfur when using the Houston Atlas catalytic conversion unit.

Separation by GC seems a desirable alternate, but a packing different from the original polyphenyl ether column in the Bendix is required. Five possibilities were considered: a longer PPE column, Triton X-305, Deactigel, Poropak R, and Poropak Q. Screening tests on these alternates led to the selection of Poropak Q for further field testing:

a) Polyphenyl ether in the original Bendix packing shows a slight separation between COS and H_2S, as a shoulder on the side of the H_2S peak when COS is added as a minor constituent. The indivudual peaks for H_2S and COS lie entirely within the time gate for H_2S alone. A double length column of PPE widened this separation significantly, after pre-conditioning with a high concentration of COS, but not far enough to avoid overlapping peaks. The double length column also gave an improved separation of CO_2/CO, but a slower response to SO_2. The use of a still longer PPE column was considered as a possibility, unless other alternates were more attractive.

b) Triton X-305 has been used regularly in these laboratories, with the Dohrmann oxidative cell as a detector, to separate COS, H_2S, and various organic sulfides. The Dohrmann cell is not subject to the CO_2/CO interference which prevents the use of the FPD sensor for sulfur compounds in stack gas samples. Several difficulties appeared with the Triton X-305. New packings from the original supplier which duplicated exactly the description of the original method of preparation did not give the same separation as retained samples of the original supply, which have been in use for two to three years. After six new samples had been tested, from two different suppliers, it developed that the new packing does in fact give similar results, but at a different operating temperature which must be very exactly controlled. A good split between COS and H_2S is obtained at 45°C, but not at either 30° or 60°. A more serious defect is that the Triton X packing does not solve the problem of CO_2/CO interference at high concentrations, so that it cannot be used in combustion stack samples.

c) Deactigel is recommended by Thornsberry and by Hartmann of Varian Aerograph (7) for the separation of COS, H_2S, and other odorant sulfides. This is a silica-based material, partially deactivated and double-washed with chromic acid and HCl for improved selectivity. Independent tests in these laboratories have indicated that Deactigel is highly sensitive to water vapor, which acts as an irreversible poison under ordinary conditions. Consultation with the manufacturer confirmed previous indications that a Deactigel packing which has been poisoned by water can be regenerated only by prolonged baking at temperatures above 250°C., and reactivation by an acid wash with HCl. It is theoretically possible to avoid contact with samples high in water vapor. This would not avoid a cumulative effect at lower concentrations, however, with a packing so easily poisoned, and other alternates seemed preferable.

d) Poropak R and Poropak Q both give a sharp separation of CO_2/CO and a good separation of H_2S, COS, H_2O, SO_2, CSH and heavier S odorants. Poropak R was tested first, but given second rating because it is slow for SO_2. It also gives an exceptionally strong response to H_2O, which is not harmful at low concentrations but strong enough to create a high background for neighboring peaks if water vapor in the sample is high. Both Poropak R and Q give a good separation for CSH, with a peak which is strong enough for stack gas measurements (1 ppm or more), although not as strong as might be desired for ambient measurements at the ppb level.

The results of this comparison are summarized in Table 25:

TABLE 25

SCREENING TESTS ON ALTERNATE PACKINGS

Packing	CO_2/CO	H_2O	Response to COS/H_2S	SO_2	CSH
PPE	Poor	None	Shoulder	Good	Slow
Triton X	Poor	None	Good	Slow	Slow
Deactigel	Good	Poison	Good	Slow	Good
Poropak R	Good	Strong	Good	Slow	Moderate
Poropak Q	Good	Good	Good	Good	Moderate

Poropak Q was selected on this basis for further tests with reduced S compounds, and in field tests at the paper mill site.

3.2.4 CSH and Heavier Sulfides

Methyl mercaptan shows a quantitative response in the Bendix, Barton, Houston Atlas and Dohrmann cells, with some qualification in each case on the interpretation of the data obtained. The same qualifications apply to the use of these instruments with heavier sulfur compounds. The RAC does not respond to any sulfide heavier than H_2S.

The Bendix instrument as supplied, with PPE packing, shows a CSH response which is just outside the 3 minutes time period allowed for sample elution, before blow-back for the next cycle. The peak can be easily found by holding the valve timing on manual control, at this point in the cycle. The choice of GC packing and elution conditions can be controlled to bring this peak within the 3 minute cycle, and this was achieved with Poropak Q. With this packing, the CSH response of the Bendix was linear through 80-90 ppm, as shown by the data in Figure 17. This is a plot of parallel test results obtained in the Barton (x30) and Bendix (x200) on a series of synthetic blends based on a gas sample of a nominal 1000 ppm. The Barton gave observed values of 86.1, 86.1 and 91.8 ppm for a nominal blend of 86 ppm. The correlation curve is a straight line which extrapolates to zero on the Bendix at 8 ppm.

The Bendix in this configuration gave entirely satisfactory results for CSH blends or samples above about 10 ppm, but no response below about 5 ppm. The intercept at a zero response indicates an adjustment required in the elution conditions and instrument pre-column, which apparently held back a constant small amount of CSH equivalent to 8 ppm in a 1 cc. sample. The CSH peak is not strong, and the initial laboratory calibrations were made at higher concentrations.

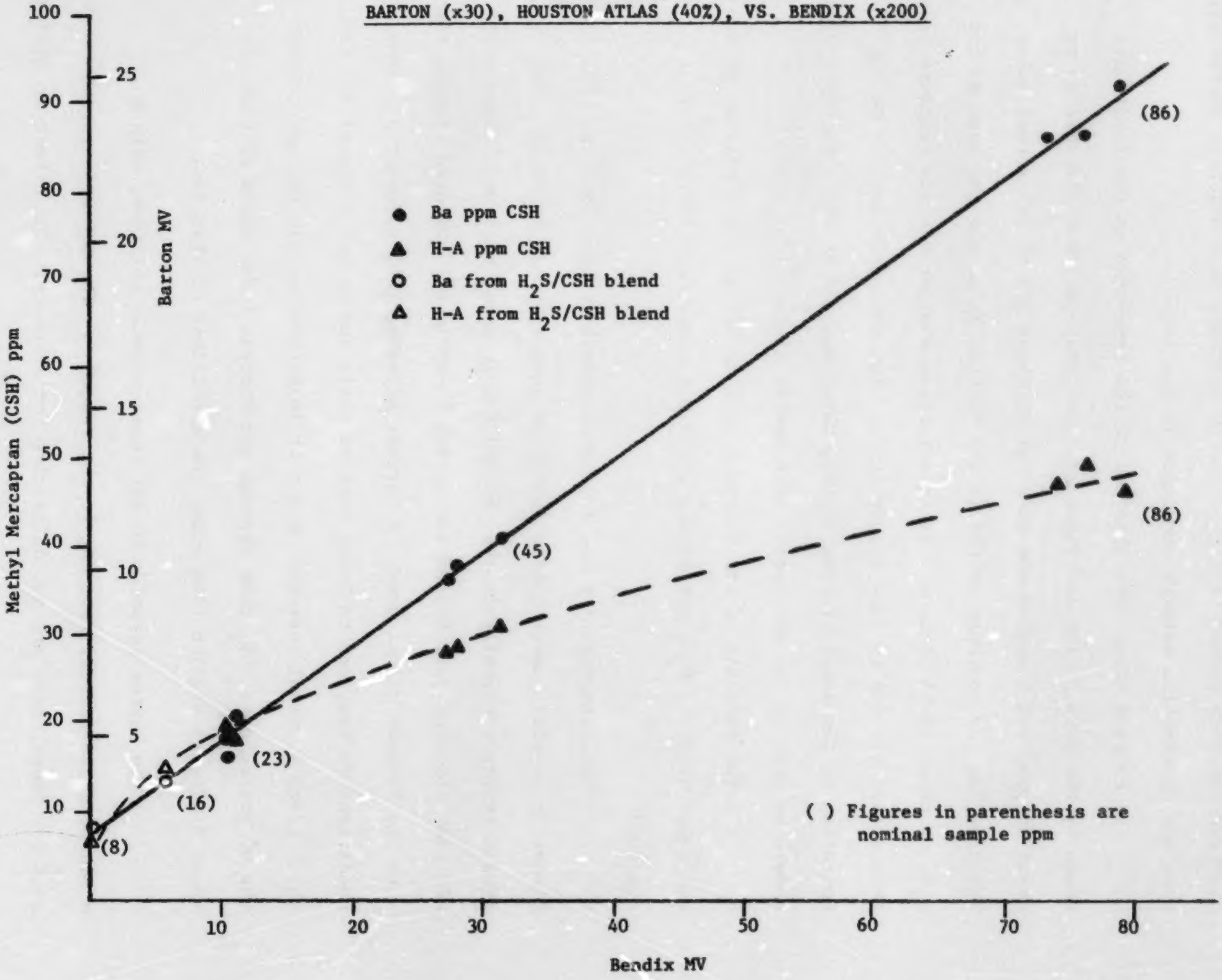
The data in Figure 17 were obtained after field tests had begun, and no changes in the pre-column were made at this time. The open circles at the lower end of this plot are taken from data obtained with an equimolar blend of CSH/H_2S, after back-calculating the H_2S contribution out of the Barton values.

A major problem of the Barton is the uncertainty of what conversion factor to use in the presence of heavier sulfides, as discussed above in Table 5. Assuming the absence of SO_2, either in the sample or after a satisfactory scrubbing, the use of the factor for H_2S (at any scale, say x10) gives results which are 40% too low if the sample is all CSH. If the sample is all SO_2 but considered as H_2S, the results are too low by 130%. The ratio for heavier sulfides is worse: the error for any CSSC present is +190%, or for CSC +300% of the calculated value.

The recommended plant procedure for using the Barton to monitor a paper mill stack gives a value "as H_2S" which is at least as high as that reported, but too low by an amount proportional to the relatively small concentration of heavier sulfides present. The accuracy of the reported value usually improves at lower values, under conditions of better control, because the control procedures applied remove the heavier sulfides more easily than they do H_2S. When heavier sulfides are suspected, the selective prefilter system used with KAP to remove SO_2 and leave H_2S (and other sulfides) can be provided with a $CdSO_4$ solution, buffered with boric acid. This removes both SO_2 and H_2S, to measure "total organic sulfides" by difference. The bubbler system requires about 15-20 minutes to come to equilibrium, however, as it does with KAP, and it gives a moving value

FIGURE 17

CSH RESPONSE, 0-100 PPM
BARTON (x30), HOUSTON ATLAS (40%), VS. BENDIX (x200)



( ) Figures in parenthesis are
nominal sample ppm

averaged for this period of time. The GC approach is considered preferable when any distinction between compounds is desired.

Houston Atlas data obtained at the same time as the Bendix are shown by the dotted line in Figure 17. The response is comparable up to about 20 ppm, and linear above this but at about 50% of the actual value. The time lag for response to CSH in the Houston Atlas was the same as for H_2S, at about 20-25 minutes. It is not clear whether the low response in this series was due to line-adsorption at high concentrations or to the operation of the sample timing sector, which was set at 40%. Further tests should be made on the new model, with heated lines.

The response of the Dohrmann cell to CSH is quantitative, on an equimolar basis to H_2S, but with a different electronic setting for each compound.

The response of these four instruments to CSH, CSC, and CSSC in blends at several concentration levels is summarized in Table 26. The Bendix responds normally to the CSH and CSC in paper mill vent lines. The CSC peak appeared just beyond the normal GC cycle of 3 minutes elution time, with the Poropak column used. A further adjustment of column/pre-column conditions is required to bring this on scale and to get a signal for CSSC, which gives a normal response on direct injection but did not get through the GC pre-column. CS_2 came through the Poropak Q far ahead of CSSC, at about 8 minutes elution time under the conditions of this test.

The Barton responds to all three organic sulfides, with no evidence of an unusual time lag in the reaction. The nominal concentrations used for these tests are not definitive for accuracy. The effect of differing

TABLE 26

RESPONSE TO CSH/CSC/CSSC BLENDS

	Nominal Blend ppm				Response (net)				
	CSH	CSC	CSSC	Scale	CSH	CSC	CSSC	ppm Scale	Remarks
Bendix (Poropak Q)	3.1	3.1	3.1	x10	0(22)	-	-		CSH erratic, at low concentration
	50	50	50	x50	65	+	-		second peak is beyond normal GC time
	-	45	-	x5	-	+	-		identifies second peak in "inlet gas"
	-	-	(*)	x5	-	-	-		no response in 45 minutes on GC
Barton	3.1	3.1	3.1	x1	70			8.9 (as CSH)	calc. 18 ppm as 3 comp. aliquot
	50	50	50	x30	47			173 (as CSH)	calc. 348 as 3 comp. aliquot
	-	45	-	x3	23			25 (as CSC)	pure compound blend.
Houston Atlas	3.1	3.1	3.1	10%	4 (10 to 30 min)			20 (as H_2S)	Shows immediate partial response, 60-80 minutes to equilibrate, readings continue after shut-off.
	50	50	50	100%	84 (10 to 40 min)			100 (as H_2S)	
Dohrmann reductive					+	-	+		normal response to 2 compounds

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* Vapor above a drop of liquid in line, v.p. ca. 10 mm Hg.
v.p. about 10,000 ppm.

factors for different compounds is noted again in the remarks, since calculated values on the aliquot basis are twice those assuming CSH alone.

3.2.5 Stack Gas Results

A primary characteristic of stack gas emissions is their highly erratic composition, both in terms of the ratio of components present and their absolute amounts. Field test data on this point were obtained both at the refinery and at the kraft mill stacks.

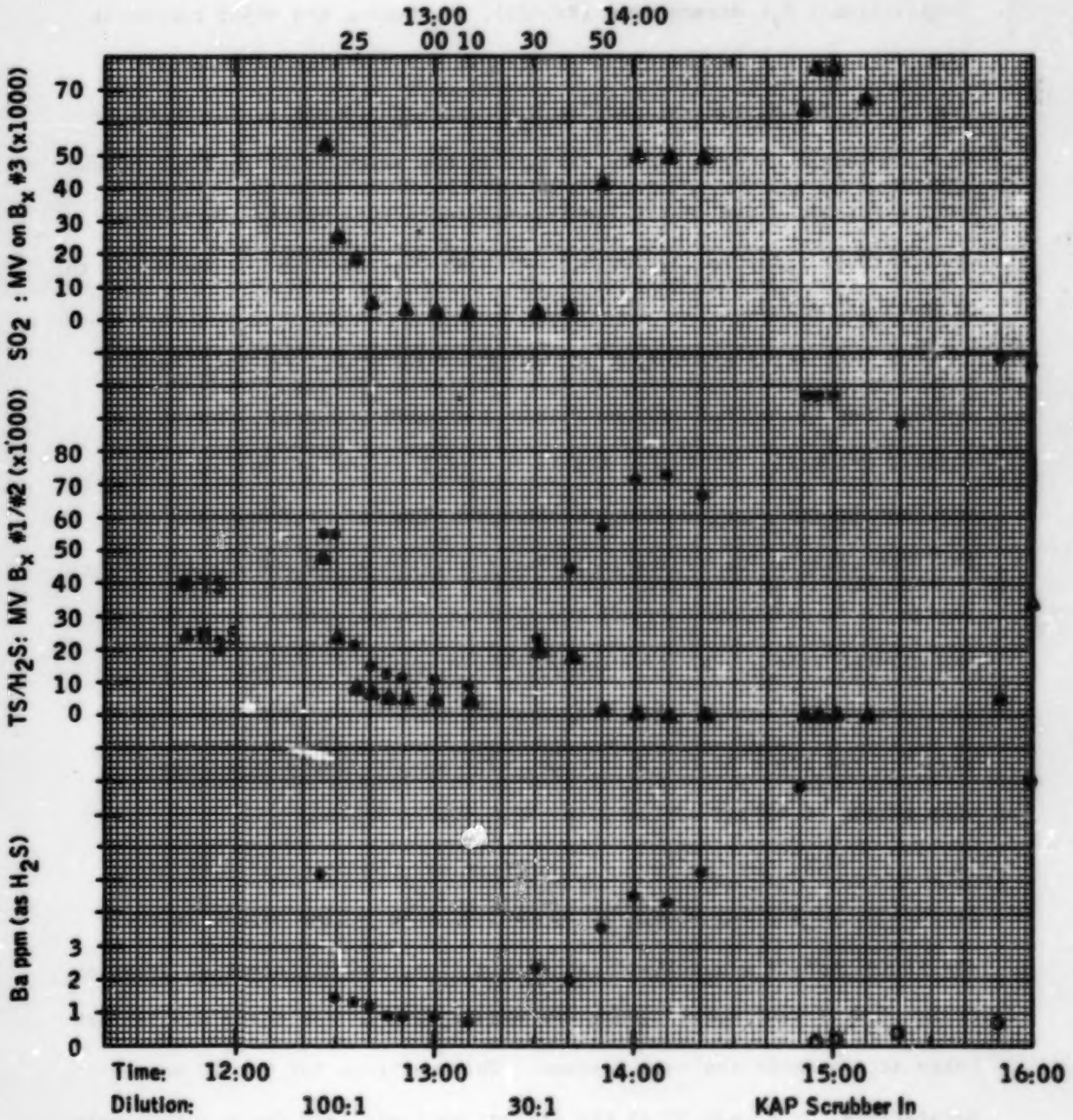
3.2.5.1 Refinery Claus Plant

Tail gas from the Claus plant as fed to the burner stack was analyzed after dilution 100:1 with air. In the first run, composition changed from 2 ppm to 6 in 20 minutes, with H_2S and SO_2 both present in about equal amounts. The sample line at the burner inlet plugged at this time, due to a slug of molten sulfur which temporarily coated the walls of the unit. The line was reamed clear of solidified sulfur and analysis continued a day later.

A second run starting at 100:1 dilution showed the results plotted in Figure 18 for Bendix total S, H_2S and SO_2, (plotted as MV) and for Barton total ppm, calculated "as H_2S". At the start both SO_2 and H_2S were present, and the Barton data curve paralleled closely the Bendix TS (Channel #1). During the first 45 minutes the Bendix TS and H_2S (Channel #1 and #2) moved closely together, but for most of this period the Bendix SO_2 (#3) went down close to zero. After 13:10 (time) sample dilution was changed from 100:1 to 30:1, to give a higher reading level and better data. A prompt increase in Barton ppm and in Bendix TS/H_2S was observed but no increase in SO_2 readings, at 3 1/3 times the sample concentration.

Figure 18

TAIL GAS FROM REFINERY CLAUS PLANT, DILUTED



Shortly thereafter, there was an abrupt change in sample compositions: H_2S disappeared (Bx #2), SO_2 became the major component (Bx #3), and the Barton curve and Bendix total S climbed smoothly together. The Barton reading "as H_2S" reached 7.9 ppm at 14:50 on the diluted sample, equivalent to 265 ppm in the stack. RAC readings at the same time, not shown in the figure, decreased to a blank. This is a qualitative indication of low H_2S, or high SO_2, or of both, which was the present situation.

At 14:52 the Barton SO_2 scrubber was placed in line. The Barton reading for H_2S dropped within 3 minutes to zero. It then climbed gradually, while the Bendix H_2S (#2) stayed at zero at first and then increased, a few minutes after the Barton, corresponding to the time delay in GC separation. Between 15:50 and 16:00 another abrupt change in composition occured: the Barton changed from 0.7 to 8.0 on the diluted sample, representing 23 to 270 ppm in the stack. Rapid fluctuations continued, with readings off scale (over 300 ppm in the stack) three times in the next hour. The sample line plugged again with a slug of molten sulfur after 10 hours on stream.

Rapid fluctuations of this type are characteristic of plant operation, during any change in operating cycle. Time delays in the analytical system are critical at such a time, and differential measurements of different constituents are meaningless unless these samples are taken at precisely the same instant. This was true for the GC sample separations, Bx #2 and #3 in the present analysis, and for no other pair of measurements obtained. The time difference was small for Bendix total S (#1), less than a minute between sample injections into the FPD sensor, but more for the Barton vs. the Bendix to allow for gas mixing vs. GC separation. It is not possible to measure Barton "total S" (+SO_2) and "H_2S" (scrubbed) closer than 3 minutes apart, which is the minimum time for 95-98% response, and full equilibration takes 10-15 minutes at higher concentrations. Simultaneous measurements of the separate constituents as provided by GC are a much more powerful diagnostic tool for operating controls than averaged values, although the averaged values may be adequate for monitoring alone.

In a third run, the sample diluted 100:1 changed from a concentration of 14 ppm by the Barton with the SO_2 scrubber in line, to 7, 20, 11, 14 and 10 during a period of 4 hours. A continuous plot of Bendix GC peak shapes during this run showed a definite shoulder for COS on the side of the H_2S peak, but not strong enough (with the polyphenylether GC packing) to be readily quantified. At the end of 4 hours with this gas mixture SO_2 was coming through the scrubber, and the electrolyte in the Barton cell was apparently exhausted. Later data suggest that this exhaustion may be due in part to small amounts of CS_2 coming through the sample at the same time as COS.

The refinery field tests concluded with this demonstration of these disturbing effects. The original plan to determine COS by difference between the H_2S readings of the Barton which sees H_2S but not COS and the Bendix which sees COS and H_2S together was rendered impossible by the interactions of COS and SO_2 in the Barton phthalate scrubber. The study of GC packings was completed and Poropak Q placed in the Bendix column before field tests were continued at the second test site.

Smooth operability of the sampling system in the burner stack or in the tail gas line feed to the burner was not achieved during the refinery test period, and the sampling system was rebuilt based on this experience.

3.2.5.2 Kraft Mill Furnace

A plot of typical data obtained during two weeks on stream at the kraft mill recovery furnace stack is given in Figures 19 and 20. In Figure 19 the Bendix was measuring H_2S, COS and CSH and in Figure 20 it had been reset to H_2S, SO_2 and CSH.

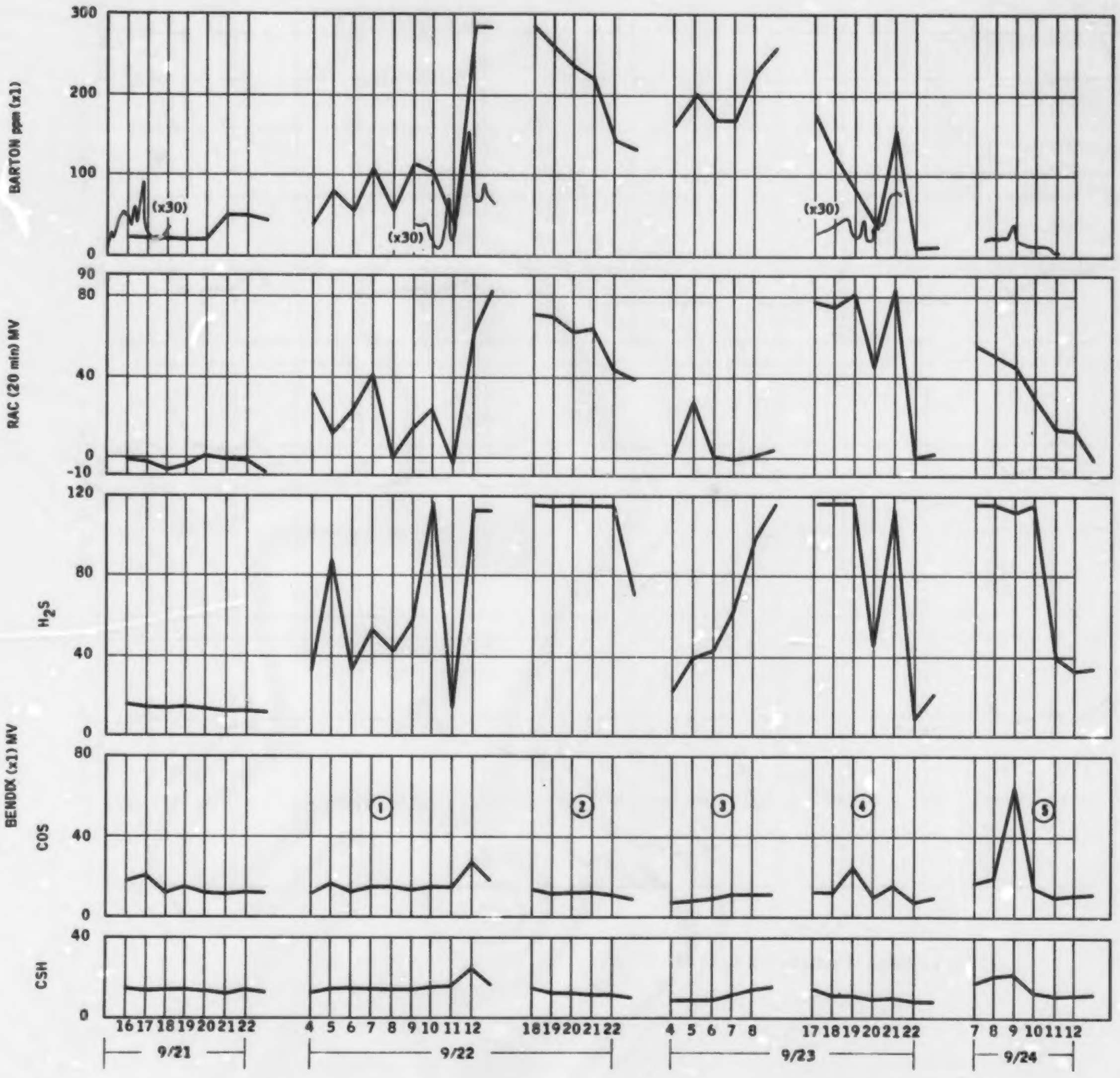
In the first two periods on Figure 19 the Barton, RAC, and Bendix all show parallel readings, with the Barton and Bendix both off-scale at the end. The composition is mostly H_2S, with some CSH, and a slight showing of COS once every 24 hours. In the third period the RAC reading goes to zero while both Barton and Bendix are high, suggesting the presence of SO_2. Readings are parallel again in periods 4 and 5, with sharp but small peaks in COS which appear in each case just before a sharp decline in H_2S.

Several interesting correlations appeared on comparing the analytical record of these COS peaks with the operating log of the paper mill recovery furnace. Significant points from this comparison are summarized in Table 27. These data were obtained during a period of unattended operation for the instrument van, with hourly readings throughout, and with no special readings or notice to the mill operators. The COS peaks were observed only once a day: 4 out of 5 times this was with the same operator, from 2 to 4 hours into the shift. For this operator, the COS peak was preceded by a sharp rise in H_2S (Barton TS) about 30 minutes

Figure 19

KRAFT MILL RECOVERY FURNACE STACK

H_2S/COS/CSH



Period

(1) parallel readings, mostly H_2S, & CSH - Bx off scale.

(2) RAC is good, mostly H_2S, Bx off scale.

(3) RAC is killed, SO_2 present, H_2S high, CSH present.

(4) parallel readings, COS appears before sharp - H_2S.

(5) Sharp COS and CSH, before - H_2S.

Figure 20

KRAFT MILL RECOVERY FURNACE STACK

$H_2S/SO_2/CSH$

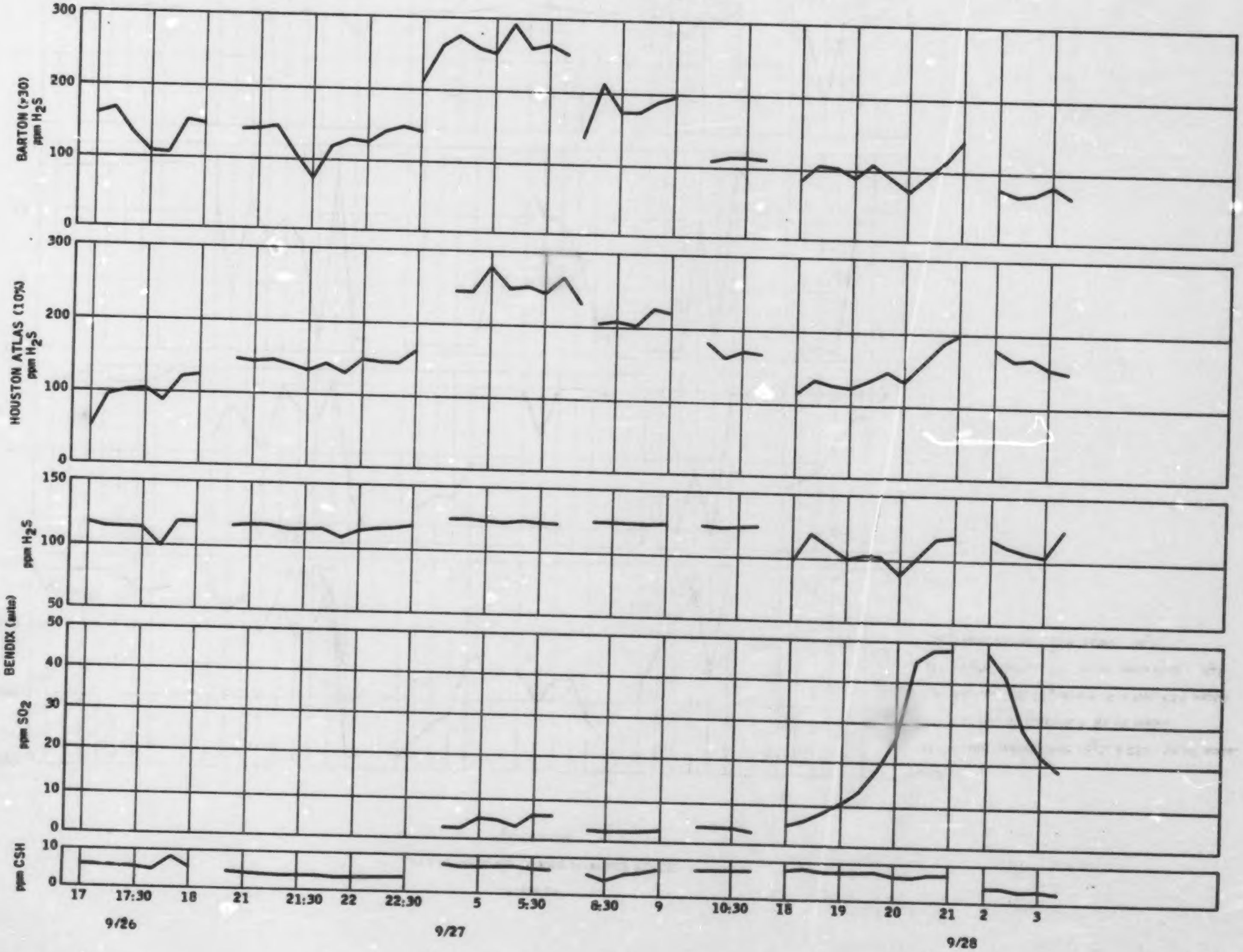


TABLE 27

CORRELATION OF COS AND MILL OPERATING LOG

			H_2S Peak History			Recovery Furnace Log: Hourly Readings				
Date	Time	COS Peak Height	Barton: TS (Continuous)	ppm	Bendix: H_2S (1 hr. Sampling)	Black Liq. Flow Rate	BL % Solids	Steam Rate	Hours After Shift Change	Operator
9/21	17:00	8.6	Sharp rise @ 16:30	50-160	level	low		sl. low	2	A
9/22	12:00	12.8	Sharp peak @ 11:30	>180	up at peak	low	low	low	4	A
9/23	19:00	13.1	Sharp rise @ 20:15	50-135	up before, down after	low	low	max	3	C
9/24	9:00	51.1	Slight rise @ 8:30	45-70	down after	low	low	sl. low	2	A
9/25	10:00	11.9	Sharp rise @ 9:00	54-210	off scale			low	3	A

COS peaks once a day, 4 out of 5 are same operator (on different shifts)
4 out of 5 black liquor flow off, % solids off, or both
Operator A: sharp rise in TS before COS peak, steam rate off
Operator C: steam rate at max, TS low after COS peak.

before the COS appeared, and this pattern moved with the operator when he changed shifts. The other COS peak with a different operator followed a different pattern, with a sharp rise in H_2S after the COS instead of before. For both operators the black liquor flow rate and % solids tended to be low at the time the COS appeared, and the accompanying H_2S peak was usually the highest reading for the day. The meaning of those data in terms of mill operation are not known, and much more information might have been obtained by taking COS readings or log data more often than once an hour. The potential value of such component analyses in the study of emission controls is obvious.

During the period plotted in Figure 20 the Houston Atlas reductive combination shows a close parallel to the Barton curve, based on total sulfur. This plot is for a week-end of unattended operation, and for most of this time the Bendix curve for H_2S is off-scale. A higher dilution ratio should have been set for unattended measurements. At the end of this period H_2S comes down on scale and SO_2 which has been moderate shows a sharp peak of about 4 hours duration. This information is available only from the Bendix GC/FPD plot. It could not be read at all from the Houston Atlas, or as reliably from the Barton plus phthalate scrubber.

Operation continued at the recovery furnace stack for a period of three weeks, including three week-ends unattended. At the end of this period the timing disc in one of the Barton probe control boxes slipped out of adjustment, apparently because it had not been adequately tightened on setting. The result was to allow air to blow back into one of the two probes as noted in Figure 14 above, creating a sharp sawtooth effect on the Barton chart and a greatly damped sawtooth on the Houston Atlas. Readings on the Bendix during this upset were erratic and useless, because of the unpredictable effect of partial air dilution in the line at the exact moment of GC sampling.

The instrument van was then moved to the lime kiln stack for further tests. This gave essentially nul point readings on all instruments, corresponding to previous data and current results in parallel obtained by a Barton unit at the plant. This stack runs very wet, with a constant rain of water condensing inside the stack and running off at the bottom. It is apparent that the lime kiln in this plant was not being overloaded and could be run at a higher loading of injected gas, if this were desirable for pollution control. Two samples of diluted inlet gas as fed from a gas accumulator to the lime kiln showed the presence of GC peaks for about 130 ppm of CSC and 35 ppm of CSH, in addition to CSSC and H_2S.

3.3 Operating Limitations

3.3.1 Instrument Advantages and Disadvantages

The eight instruments from six manufacturers which were examined in this study each had advantages and disadvantages. These are tabulated for convenience in Table 28, in five pages for different instruments: the Barton, Bendix, Houston Atlas (pyrolytic unit), RAC (and simple Houston Atlas), Dohrmann (two cells) and Philips. The

TABLE 28

EVALUATION OF INSTRUMENTS (BARTON)

Advantages	Intrinsic Disadvantages	Operating/Maintenance Problems
Barton (Coulometer)		
1. Simple operation, adequate instructions.	1. Response coefficient differs greatly for different odorants, difference changes with range. H_2S gives approx. 4x response of RSR for same ppm, H_2S/SO_2 approx. 2.3x, H_2S/mercaptan 1.4x. SO_2 scrubber solution is inoperative with SO_2 + COS.	1. Probe operation can be improved by longer blow-back, alternate operation of two probes is better.
2. Field tested, long unattended runs, long cell life, slow chart speed.	2. Cell is poisoned by CS_2, in high amounts or cumulative.	2. Correction for water in stack samples is a source of error, usually assumed constant or ignored.
3. Wide ranges of total sulfur, responds to S of 5 types; fast response: 0.3 to 1000 ppm, slow response: 0.01 to 10 ppm. Operates satisfactorily overrange.	3. One-liter surge tank used to knock out water in sample introduces a 15-20 minute delay in response.	3. Cleaning cell or bubbler when frits are clogged requires laboratory facilities, not convenient for the field.
4. Little attention required, solutions last up to 30 days.	4. Flowmeter provided is not nearly adequate to measure actual flow, (reading-dependent); used extra rotameter, manometer and pump.	4. Normal maintenance schedule must be changed if unusual samples appear.
5. Control box can be remote from cell, electrical connections only. Aspirator system on cell vent is good (Br_2 corrosion no problem).	5. Flow rate to aspirator is sensitive to very small pressure changes; "auto cycle" SO_2 scrubber can cause a 10% drop in H_2S readings.	5. Importance of cell temperature control increases for lower readings, requires air conditioning for accuracy.
6. Electronic stability good, two cells well matched (0.98 and 0.99 of theoretical output).	6. No clear indication when electrolyte in cell is depleted, varies with loadings; shows up in cell blank, which must be adjusted after each refilling.	
7. Field-tested sampling probe.	7. Zero and readings change with ambient temperature.	
	8. Slow circulation of cell electrolyte causes rapid cycling of cell readings, between limits which are progressively further apart at lower ranges; cell equilibration time becomes 20 minutes at x1, 2 hrs at x.3, 8-16 hrs at x.1.	
	9. Fritted distributor discs in cell or scrubbers get clogged with sulfur formed in sample lines.	
No improvements announced.	10. Wet chemical bubblers supplied to separate 5 gases require at least 20 minutes to equilibrate: still a research-type measurement, not quantitative under field conditions.	

TABLE 28

EVALUATION OF INSTRUMENTS (BENDIX)

Advantages	Intrinsic Disadvantages	Operating/Maintenance Problems
Bendix (GC/FPD)		
1. Measures separate components directly.	1. FPD interference from CO/CO_2 in stack gas amounts, or hydrocarbon in process effluents, prevents total sulfur reading in these streams; requires different GC column for this use.	1. Not yet ready for an unskilled attendant.
2. No wet chemistry.	2. Rotameter not accurate enough for sample flow control; flow rate changes with gas temperature, limiting on reproducibility.	2. Needs a better instruction handbook.
3. Readings held in memory circuits, readout cycle 15 minutes for 3 gases (4 possible), or on demand.	3. H_2 flow is critical, to hold flame; rotameter not reproducible. Needs a separate shut-off valve.	3. Manual zeroing better than automatic; adjustments not adequately explained.
4. GC exceptionally reproducible, versatile as to sample size, gating; timing holds well for months.	4. Electronics optimized for ambient range, needs different balancing for emissions range.	4. Needs flow controller, or needle valve plus manometer.
5. Designed for easy adjustment, repairs, or substitution of GC columns.	5. Need readable potentiometers to adjust gating, time cycle, oven, attenuation, etc.	5. Mechanical failures in valve diaphragms, needle valves, one soldered joint.
6. Teflon lines and valves.	6. Zero stability good short term but high long-term drift; adjustment very sensitive, not easily controlled.	6. Oven temperature not easily adjustable; fiber optics vulnerable on runaway.
7. Safety features for flame-out.		7. Automatic attenuation gave variable zero levels, needs internal balancing with rates and times.
8. Good field service when required, good diagnosis on phone calls.		8. Reignition should not require change in flow settings.
9. Field tested (for ambient only).		9. Needs indicator on valve-actuating pressure line.
Improvements Claimed During 1972		
1. Automatic flow control for reignition.		
2. Positive sample flow control.		
3. Fiber optics in FPD replaced by insulated direct mounting.		
4. Rapid automatic zeroing.		
5. Readable external potentiometers.		
6. New valve diaphragms, longer life.		
7. Improved oven temperature control.		

TABLE 28

EVALUATION OF INSTRUMENTS (HOUSTON ATLAS 855)

Advantages	Intrinsic Disadvantages	Operating/Maintenance Problems
Houston Atlas 855 (conversion to H_2S, Pb tape) 1. Pyrolysis + catalytic reduction converts all S compounds to measurable H_2S.	1. Excessive time lag in response, average 30 minutes, attributed to gas mixing in conversion chambers; concentration pulses dampened when they do appear.	1. Prompt field service and supplies, but no instructions or handbook available.
2. Only field instrument which gave a true total S reading.	2. Small diameter stainless lines selectively retain and later release SO_2 or heavy S cpds (RSSR).	2. Photocell fatigue and lint from moving tape build up imbalance, beyond bridge adjustment; requires periodic cleaning and readjustment.
3. Simple controls, few adjustments of any type, good flow valves.	3. Flowmeters inadequate, range adjustment poor, time setting for dilution not too accurate.	3. Dilute acetic acid bubbler may be either depleted or flooded by radical changes in sample humidity; tape breakage can result from an unexpected increase in sample water content.
4. No electronic problems.	4. Two-stage dilution with single timer (optional), can cause pulse flow and exaggerated artificial swings in concentration observed.	4. Recorder unsatisfactory; hard to read or write on, needle broke in service and gave double readings.
5. Sample preconversion system could be used with better sensors.	5. Problems inherent in $PbAc_2$ tape recorder: humidity control to get reaction, too much water wets tape and causes breakage; moisture on windows changes zero levels; variable zero on tape reflectance ±2% average, but spikes of −10%; changes ±3-5% from one tape to another.	
6. Ag tape available, not sensitive to SO_2.	6. No indication when tape has run out or broken, could use an optical signal or tension switch.	
Improvements Claimed During 1972	7. Significant H_2-consumption, some is vented; running without H_2 harms catalyst activity, needs an automatic shut-down.	
1. Delay in response time cut (4 minutes modulus), by redesign of conversion chambers.		
2. Accurate sample control valve and metering, better recorder.		
3. Spray carryover to tape from humidifier corrected.		
4. All process flow lines heated (200°F); greatly reduces hold-up of polar constituents.		
5. Tape zero problem avoided by new sensing system: measures rate of reaction (slope), feeds continuous signal to digital storage for timed average.		

TABLE 28

EVALUATION OF INSTRUMENTS (RAC, HOUSTON ATLAS 825)

Advantages	Intrinsic Disadvantages	Operating/Maintenance Problems
RAC (Tape Recorder)		
1. Simple system, few adjustments, for H_2S only (ambient range).	1. $PbAc_2$ tape cannot be used for most stack gases; reaction killed by SO_2, must be scrubbed. Narrow response range is too limited for widely varying samples.	1. No handbook, instructions incomplete: considered a standard AISI unit using $PbAc_2$ tape.
2. Simple procedure for dilution: cumulative reading affected only by flow of sample and not by exact control of dilution gas.	2. Uses only lower half of logarithmic scale; ± 15-30% accuracy claimed, depends on concentration.	2. Tape zero system limits already narrow range, frequent cleaning to remove lint from optics: gave continual trouble using samples of widely varying range, with rapid tape consumption.
3. Enclosed model recommended, if odorants present other than H_2S.	3. Stack concentrations require high dilution with a carrier gas (not ambient air, or plant air, if it contains any S).	3. Mechanical operation otherwise very good.
4. Case well designed for routine maintenance, parts accessible.	4. System of exhausting treated gas into case not recommended, except for ambient use.	4. Slow supplies, service average.
	5. Variable concentrations handled only by change in flow or cycle time; high levels and short times use up more tape.	
No improvements announced	6. Humidifier chamber must be watched, too little = no reaction, too much = overflow. H_2O supply lasts 1-2 days with dry dilution air.	
	7. Tape zero changes rapidly during warm-up: stability poor when pushing limits, may be more stable in routine operation, for limited range in known environment.	
Houston Atlas 825 (Tape only)		
1. Does not see S compounds other than H_2S and SO_2.	1. Usual problems of $PbAc_2$ tape (see above).	1. Instructions needed, both for normal operations and for adjustments.
2. Acetic acid bubbler can tolerate limited SO_2 exposure (reversible).		

TABLE 28

EVALUATION OF INSTRUMENTS (DOHRMANN, PHILIPS)

Advantages	Intrinsic Disadvantages	Operating/Maintenance Problems
Dohrmann (Microcoulometer)		
1. High accuracy, if calibrated by matched samples (differential analysis).	1. Has to be checked every day for standard, using same gas and similar concentrations, and restandardize for each major change in sample.	1. Instructions provide nothing on general trouble-shooting: limited to research papers describing specific uses and precautions.
2. A basic sensor device, adaptable to different systems of sample preparation.	2. Range and standardization change with sample size, more critical at higher readings.	2. Requires skilled supervision.
3. Reductive cell (Ag) does not see SO_2 and responds only to H_2S, CSH, COS (in absence of chloride or cyanide).	3. Critical adjustments of electronic bias, gain, and range required for each different sample.	3. Set-up time an hour each day.
4. Oxidative cell procedure converts all S compounds to SO_2 and measures this.	4. Readings affected by cell temperature, stirring rate.	4. Service fair in emergencies, normal supplies slow.
	5. Laboratory facilities required, in the field: distilled water and sink, drain and flush cell; standard solutions renewed daily; gas blending system for calibration samples; "standard sample" gas handling procedures; daily handling of fragile glass cell.	
	6. Oxidative system furnace requires cooling water.	
	7. system consumes the electrode; slowly for spot samples, more rapidly at high concentrations, critical in continuous service.	
Philips (SO_2 Monitor)		
1. Excellently engineered (for ambient range).	1. Chemical filter supplied to scrub SO_2 out of H_2S ($BaAc_2$) has limited capacity, not adequate for stack concentrations.	1. Excellent manual of instructions, informative and easy to use.
2. Adaptation to H_2S (ambient) can be extended to max 3-5 ppm.	2. Max H_2S range is too low for stack emissions.	2. Field service extremely slow on anything except routine servicing, which is good.
Improvements Claimed for 1972	3. Dilution has to be accurate, if used, since reading is of concentration and not cumulative amount.	
1. Separate modules for SO_2 or H_2S; same limits on maximum concentration.	4. Unit has low tolerance for samples under pressure.	

first column for each instrument lists advantages observed in use. Intrinsic disadvantages are considered inherent in the present design and construction of the equipment. Operating and maintenance problems encountered reflect the quality of the manufacturers' service and operating instructions.

It should be emphasized that the statements made are based largely on the study of a single instrument, which was on loan from the manufacturer and not purchased. They might or might not hold true in exactly the same form for another instrument. These statements were discussed with the manufacturers from time to time throughout the program and confirmed by them as valid general observations. Improvements to correct or eliminate many of the problems noted were made during the year by Bendix and Houston Atlas, and to some extent by Philips. These are listed in the first column on each page as a second heading, under Advantages. Certain major points can be noted from the Table for each instrument.

The Barton Titrator is simple to operate, has good instructions, a wide linear range, and can be used for rapid direct measurements in stack gases from 0.1 to 1000 ppm. The lowest two attentuation scales (x.3 and x.1) are very slow to come to equilibrium, unless the inner cell electrolyte is dumped out by hand for forced circulation, and measurements below 0.1 ppm should not be considered routine. The Barton is good for either H_2S or total S (as H_2S), in the absence of significant amounts of COS or CS_2. It can also be used with chemical bubblers on a research basis to measure individual components, but this is not suitable for routine use in the field. Even the simplest of these chemical separations, SO_2/H_2S, is only 85% quantitative in the 1-10 ppm range: it cannot be relied upon at this level to indicate the absence of SO_2 in H_2S or vice versa. This SO_2 bubbler must be avoided when COS is present.

The Bendix unit analyzes for individual compounds, without chemical separation. It is stable and reproducible over long periods of time in GC sampling, timing, and in zeroing as compared with the other instruments. The design and construction of the instrument is being actively improved, with better instructions, and is further along than the similar instruments manufactured by Tracor or Varian Aerograph. The original GC packing of polyphenyl ether cannot be used with the FPD sensor on stack emissions that contain percentage amounts of CO, CO_2 or hydrocarbons. Good results were obtained with Poropak Q, and GC packings can be changed in the field if desired. This is better done at the factory, however, since it is likely to require a careful rebalancing of electronic controls to get proper operation of such features as automatic zeroing or automatic attentuation.

The Houston Atlas pyrolytic/catalytic reduction unit is basically sound, and gives a true reading of total S compounds. The very long time lag in the unit under test prevented a good evaluation, but this was apparently due to the fact that this was a prototype. The instrument can use better controls, auxiliary equipment and instructions. It is considered promising for further development, and many improvements along these lines have been made during the year.

The RAC and simple Houston Atlas $PbAc_2$ tape recorders measure H_2S only, and cannot be used for more than a very limited time in the presence of SO_2. The RAC has less tolerance for SO_2 than the H-A, which was not evaluated in as much detail. Both units need operating instructions: this lack was particularly troublesome in trying to adapt what is essentially an ambient range procedure for use in stack gas measurements. The logarithmic reading scale and narrow range at a given setting of the RAC are undesirable. Somewhat better results might have been obtained by running it at a much higher dilution, which means using more carrier gas and fewer samples analyzed per hour. This should cut down the high frequency of cleaning and adjustments required to stay in operation with samples above 1 ppm.

The two Dohrmann cells are essentially research type instruments. They can be used for an absolute calibration procedure in the laboratory, in electrochemical equivalents. The reductive cell has a further advantage in not responding to SO_2, while it measures H_2S and mercaptan. Requirements for constant recalibration and adjustments are far too complex for routine operation, however, and not really suitable for use in the field. The absence of interfering chloride and cyanide in small amounts is also not to be taken for granted in petroleum refinery stacks.

The Philips Monitor is a good instrument, but its upper limit of adjustment at 6-10 ppm of SO_2 corresponds to only 3 ppm or at the most 5 ppm of H_2S. It also requires chemical filters for any distinction between sulfur compounds. This concentration range is of little value for direct measurement of stack gas samples.

3.3.2 Data Logging Limitations

The Esterline Angus system was plagued by mechanical problems which resulted in some 30 service calls during the year, and were never fully diagnosed in the field. These were largely in the electronic system, and not in the replaceable printed cards. Some of them at least were due to troubles with internal grounding, and others were due to cold soldered joints which gave intermittent open circuits.

Three different E/A units were finally supplied before satisfactory operation was achieved. The first one gave occasional false readings in specific channels, which were traced to grounding. It subsequently began "machine gunning" a series of overprinted characters, all on the same line. Tapes containing such a record stopped the IBM 1130 as illegal characters, which could not be read. This defect developed gradually over a period of weeks, and finally became chronic. It was not repairable in the field by putting in either new circuit boards for the printer or a new printer, and the unit was returned to the factory.

The second unit behaved normally at first, then began printing occasional zeros only instead of the proper reading. This malfunction began on a day when the trailer van was hot, because the air conditioner was off. It stopped when the air conditioner came on temporarily, and it was then found that a small cooling fan directed at the E/A unit stopped the zeros. The same pattern repeated on later days when the zeros appeared at normal van temperature, and the cooling fan was kept in use, directed at the power pack inside the case.

The unit next developed a failure in the timing circuit, which reset itself to a lower value each time it came to 22:40 on the clock. This was corrected by finding loose soldered joints. The unit then developed a pattern of showing an occasional extra 100 or 200 digit in the first nixie display, for less than a second, on switching to a new channel. The momentary reading could be caught and recorded if the printer happened to hit that specific second in its cycle. This began to occur about once in a thousand readings.

The original E/A unit was finally reworked completely by the factory, and run in parallel with the second one during the paper mill field test, as a double check against each other in case of unexplained variations. This third unit was placed on line alone for the last eight weeks of the program and showed no mechanical failures during that time.

Two minor recommendations were made for improvements in the design of this equipment. The first of these, which was incorporated in the next production models, is a control switch which makes it possible to select or not select individual channels which are printed on the tape, instead of printing all channels up through any one selected. A second desirable modification would provide the capability to print an index character on demand, to mark the end of data or some special comment in the operating notes.

The Tally punch gave no problems, other than printing an illegal character when it received a false signal from the E/A. It was recognized, after the fact, that the IBM might have been programmed either to accept and by-pass these signals, or at least to be able to restart the tape and continue at the next reading after it was stopped, instead of losing the whole print-out or manual reading of the tape.

3.3.3 Sampling System Limitations

The mechanical problems which had to be overcome in the sample probes and pumping system were primarily related to the large amount of water present in the stack gases selected for testing. Excess water, in variable amounts, is no longer a limitation in the system as finally built. The original design had separate timers operating in parallel, which are not easy to keep in phase with each other. The final design with a single timer is much simpler to adjust and operate. The Barton stainless steel probes with integral glass fiber filters proved suitable for severe service with air blow back. Simpler probes may be enough under less severe conditions, depending chiefly on the nature and amount of the particulates present.

Operating the gas sample manifold to maintain a constant gas pressure with variable demand requires a slight overpressure, to avoid short-term changes in line pressure with changing demand. A manifold gas supply of 650 cc/minute when using 500 cc or less was enough to maintain the manifold pressure constant at 108 ± 0.5 mm. A simple but sensitive pressure relief valve is adequate. The principal operating problems were the failure of gas pumps and needle valves in individual instruments, as noted in Table 28. The use of good valves and calibrated flow meters in the blending system is essential to successful operation. The three mass flow meters in parallel used to feed calibration gases into the manifold are very sensitive to line pressure, and a change of 5% or more in setting for any one of them required a minor adjustment in the others to maintain a constant flow rate.

Operating the gas manifold under pressure creates a problem in feeding synthetic gas blends, which are conveniently made up using calibrated syringes and known volumes of gas. A suitable system for this was devised using hydrostatic pressure, in a 5 gallon paint can containing a Mylar gas bag. With water emptied out of the can, the gas bladder was evacuated and then inflated at atmospheric pressure with the desired blend, made up in a 10-liter Houston Atlas acrylic gas-blending cylinder. The can surrounding the bag was then vented to the air, and refilled with water under a 15 foot head. This created a pressure drive of 8 psig, under which the sample was fed through a mass flow meter into the manifold.

Operation of the permeation tube system in a water bath at 30°C was not easy to maintain in the trailer van, without a ready supply of cooling water. The use of a themostatically controlled air bath at 35°C or 40°C is recommended as a preferred procedure. Satisfactory results were obtained in the laboratory using air bath units of limited capacity for H_2S at 35°C and SO_2 at 40°C. Improved equipment of this type is now available from Analytical Instrument Development, Bendix, and several other manufacturers. A carbonyl sulfide permeation tube was also tested, but its useful life was limited to less than 3 weeks which is too short for convenience.

4. GENERAL CONCLUSIONS AND RECOMMENDATIONS

4.1 General

None of the instruments commercially available was able to provide a routine analysis at emission levels for H_2S/TRS, or for individual S compounds, in both the refinery and paper mill test. The differences between ambient monitoring and stack measurements for odorants had not been adequately considered by the manufacturers as of the start of this program in 1971, or recognized in their manuals of instructions.

The lack of adequate instructions is clearly significant, in any program for instrument evaluation. It suggests either limited resources, inexperience, or a lack of understanding on the part of the manufacturer. The company may be too new, or too small to afford the expense. A poor manual, however, must be recognized as a signal that the user is on his own, and that the manufacturer may not really know yet how to keep the instrument working when it runs into trouble.

The problem of what to measure in odorant emissions has changed in the last few years, with the advent of simple pollution controls in the plants most subject to complaints. There is less of the odorous mercaptans and higher alkyl sulfides, which means H_2S is more useful as an indication of total reduced sulfur. At the same time, the ratio of other inorganic sulfur compounds to H_2S may increase markedly in the remaining gas, so that there is 10 to 1000 times as much SO_2 (or COS) as the odorant H_2S left to be measured.

The choice of which instrument is best depends in part on what source is to be analyzed, and in part on how well improvements made by the manufacturers during 1972 work out in actual practice. Specific recommendations are made for possible further developments on the three instrumental approaches which were found most promising.

The preferred approach where individual components are of interest is the combination of GC/FPD. Coulometric titration, however, is the only method which has been extensively tested in the field. The chemical filters on which this method depends for component analyses have limitations which depend upon the source to be measured.

4.2 Barton Titrator

The Barton coulometer has given satisfactory field service for years in a number of kraft paper mills. They can use its results as differential measurements for control purposes, without having to determine the composition of the odorant mixture. This success is due in part to the fact that the odorants present have a fairly constant composition and consist predominantly of reduced S compounds, with H_2S in excess, a variable small amount of SO_2, and little or no COS/CS_2. The lack of an exact zero means that the Barton cannot give absolute values. Readings are also directly proportional to sample flow rate, which is not accurately and continuously measured in present plant practice. The addition of a flow rate controller is recommended.

The dependence of the Titrator on chemical bubblers is a distinct disadvantage. The phthalate SO_2 bubbler absorbs a small amount of H_2S, amounting to 10-20% of the sample in the range of 1-10 pp, and it gives no indication when it has become exhausted. This becomes critically important when the stack gas composition is swinging from an excess of one gas, through zero, over to an excess of the other. The system cannot be depended on to define the amount or absence of either H_2S or SO_2 at 1 ppm or less in the presence of 10 ppm of the other. This type of change which is rare in kraft mill stacks is common in the gases from other sources, such as a Claus plant afterburner. The KAP bubbler fails completely in this mixture, which contains significant amounts of COS and CS_2. The failure cannot be ignored, since the interaction of COS and the phthalate solution releases SO_2, hydrodrolyzes some COS to H_2S or CS_2, and exhausts the activity of the electrolyte in the Barton cell. The Barton does not respond to COS as such but it is slowly poisoned by CS_2, in an anomalous reaction which appears to continue after the sample flow is stopped.

Research on the chemistry involved in the COS/SO_2/KAP interactions is recommended. The reasons for these effects are not entirely clear, and the results might lead to improved scrubbing procedures. Until they are available, the Barton system cannot be used to measure either total S or total reduced S compounds correctly in the presence of SO_2 and COS or CS_2. There is no assurance that any system better than KAP can be found, however, and improvements in its use may be more promising than the search for alternates.

The Barton can, of course, be used with other methods of separation such as GC, or pretreatment to convert other S compounds to SO_2 or H_2S. The usual procedure to use the factor for H_2S in measurements and report the results as H_2S is a useful compromise, but it gives no absolute values.

Research on the effect of improved circulation of the electrolyte in the sensor cell is also recommended. This could lead to a more stable zero, more accurate measurements at low scale readings, and more rapid equilibration at the lower attenuation scales. The very short term variations in cell readings attributed to uneven circulation make the Barton much less suitable for electrical recording than for reading on a visual chart. Electronic integration or averaging is a possible alternate approach for this particular problem.

There is no coulometric instrument available which combines the wide range of the Barton, the stability of the Philips, and the precision of the Dohrmann cells. Specific suggestions have been made along these lines which remain to be implemented.

4.3 Bendix Environmental Chromotograph

The Bendix GC/FPD combination has a more stable zero than the Barton, and the response of the two instruments to gases to which both are sensitive is similar in accuracy, stability and linearity up to about 80 ppm. The Bendix is superior in stability, but limited in linearity by the intrinsic response curve of the FPD sensor. Data obtained in this program indicate that with a 1 cc sample size the upper limit of linearity varies with the compound at 30-50 ppm for COS compared to 80-120 ppm for H_2S, SO_2 and CSH (methyl mercaptan).

The 80-30 ppm range is high enough for direct measurement of stack gas concentrations at the legal limits of 10 ppm or 17.5 ppm set by recent legislation in several states, and higher concentrations can be measured by appropriate dilution.

The separations obtained in this instrument depend upon the GC component: the polyphenyl ether/H_3PO_4 on Teflon supplied by the manufacturer cannot be used to measure ppm quantities of S compounds in stack gases containing percentage amounts of CO and CO_2. Good results are obtained using a packing of Poropak Q, which separates H_2S, COS, SO_2, CSH, CSC, and CS_2 and is not swamped by CO and CO_2. The system must be internally rebalanced for proper operation of automatic zeroing and automatic attenuation when any change in GC packing is made.

The instrument model tested in this program requires skilled maintenance, and it would need rebalancing every six months for optimum operation. Numerous improvements made by Bendix and other manufacturers of similar instruments during the year are intended to give better long-term stability. This needs to be confirmed by further testing.

Additional development work is recommended on modifications to permit the analysis of more concentrated samples, up to about 0.1% of H_2S/SO_2. This might be accomplished by using one of the present two valved sample loops for the purpose. The use of smaller sample size by micro-injection or an equivalent procedure such as a GC sample splitter is recommended as a desirable alternate. This or a built-in dilution system could extend the useful range of the instrument by a factor of 10 to 20 or more with no significant loss in accuracy, to cover the entire range of interest for S odorant emissions.

4.4 Lead Acetate Tape Systems

The Houston Atlas system for sample pyrolysis and catalytic reduction to H_2S is promising for further development, and suitable for use with a simple tape sensor. The instrument tested here was a prototype which suffered from a 25 minute time lag, attributed to oversized conversion chambers and small unheated lines. This interfered with its evaluation, but operation was basically satisfactory. Many improvements were made during the year, which are still to be tested in the field. One improvement which may help to eliminate the problems of zero drift is a new method of sensing which measures the rate of color change in the tape, rather than its absolute value.

The Houston Atlas pyrolytic/catalytic system could be used equally well with other sensors, such as a re-engineered coulometric cell. Present indications are that for gases free of massive amounts of SO_2 or COS, coulometric titration after converting all S compounds to H_2S should provide a good monitoring system.

4.5 Minimum Requirements for Future Instruments

The nature of the problem of monitoring sulfur containing odorants in stack emissions has been redefined, herein. It now appears that an instrument for this purpose should be capable of monitoring total reduced sulfur compounds, or H_2S alone as an alternate, in the presence of SO_2, COS/CS_2, CSH, heavier S odorants and indeterminate amounts of CO_2, CO, and water vapor. Minimum performance requirements can be set for such an instrument:

1. Linearity, stability and reproducibility of ± 2-5% or better, which are adequate in the present Bendix and Barton instruments.
2. Conversion from MV to ppm should be linear to ± 3% of scale. It can use different factors for different parts of scale but this should be minimized.
3. Response time needed of 90% in 5 minutes or less, 98% in 15 minutes.
4. Direct reading capability for the concentration range .1-30 ppm is of primary interest for odorant pollution control.
5. Reading directly or with built-in dilution for the usual emissions range of 0-300 ppm or more, with a precision of ± 2-5% of scale.
6. A positive distinction between H_2S and SO_2 at .1 to 30 ppm is required for monitoring odorous combustion stacks.
7. Significant advantages are recognized for an instrument using GC or an equivalent separation procedure which will permit the simultaneous analysis of 3 or 4 selected S compounds, including SO_2 and reduced S compounds, as odorants or as key components for odor control.

8. Satisfactory freedom from interference (e.g., ± 10% of measured values) must be demonstrated, for the sensor and for auxiliary filters or separators required, at high ratios of the interferent gases (including SO_2, CO_2, CO, and H_2O) up to 10,000-fold and COS up to 10-fold the amount of H_2S or other odorant to be measured.
9. Construction and engineering rugged enough for field use, by skilled non-professional personnel with occasional technical supervision.
10. A manual of instructions is required with an outline of trouble-shooting procedures which will enable the user to keep the instrument in operation for a prescribed warranty period (at least 6 months to a year), without special maintenance by manufacturers' representatives.

For reduced systems where the amount of H_2S/TRS is high relative to SO_2 or SO_3, the ability to give either a simple total S or total reduced S measurement with high reliability and consistency would appear to be prime goals. The non-uniformity of response to different S compounds which is a major drawback of coulometric titration could be minimized by some sort of pyrolysis/oxidation/reduction unit. The reductive unit developed by Houston Atlas appears more rugged at this point than the earlier oxidative unit offered by Dohrmann. Either approach can convert all sulfur to H_2S (or to SO_2) for coulometric analysis. Further developments are recommended along the line of a Barton or Dohrmann cell of improved stability, or a Philips cell of much wider range.

Similarly, for total S, the improvements undertaken over the past year by Houston Atlas in the detector system of their lead acetate paper tape sampler may result in an economical measurement tool of improved reliability. Further evaluation of the improved models is recommended.

A major emphasis must be placed on the evaluation of sampling systems which will operate in stack gases containing high amounts of water and particulates. The rapid separation method developed in this project is one approach, and several systems using the diffusion of water vapor through permeable membranes have become available since 1971. This problem is particularly important for the measurement of odorous H_2S at ppm levels in the presence of percentage amounts of moist SO_2, to avoid the rapid interaction of H_2S with SO_2 in adsorbed or liquid water. On this basis, both approaches appear to work.

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PAGE 1 **APPENDIX I PROGRAM 1: TAPE READING**

```
// JOB

LOG DRIVE   CART SPEC   CART AVAIL  PHY DRIVE
  0000        0010        0010        0000

V2 M10  ACTUAL 16K  CONFIG 16K

// FOR
*LIST ALL
*ONE WORD INTEGERS
*IOCS(PAPER TAPE,DISK)
*IOCS(1132 PRINTER)
*NAME ARG1
      INTEGER Q(11)
      REAL IMV(21)
      DIMENSION NZER(5)
      DEFINE FILE 1 (300,45,U,JREC)
      DATA Q/11*0/
      DATA IMV/21*0.0/
      DATA NZER/999,4*1/
      JREC=1
      DO 1 I=1,300
      WRITE(1'JREC) NZER
    1 CONTINUE
      JREC=1
      CALL SAVE
      IROW=0
   10 CONTINUE
      IROW=IROW+1
      IF(IROW-301) 12,100,100
   12 READ(4,200) IDAY,IHR,IMIN
      JCOL=0
      DO 80 J=1,21
      READ(4,210) Q
      IF(Q(1)-7744) 15,90,15
   15 JCOL=JCOL+1
      IF(Q(4)-24640) 20,50,20
   20 CALL TRRED
      READ(4,220) D1,IMV(J),D2
      GOTO 80
   50 CALL TRRED
      READ(4,250) D1,IMV(J),D2
   80 CONTINUE
   90 CONTINUE
      WRITE(1'JREC)IROW,IDAY,IHR,IMIN,JCOL,(IMV(J),J=1,JCOL)
      GOTO 10
  100 CONTINUE
      WRITE(3,270)
  200 FORMAT(I3,I2,1X,I2,2X)
  210 FORMAT(11A1)
  220 FORMAT(A3,F5.1,A2)
  250 FORMAT(A3,F6.1,A2)
  270 FORMAT(T5,'THE NUMBER OF ROWS HAS EXCEEDED 300.EXECUTE THE PRINT
     2PROGRAM AND RESTART THE READ PROGRAM')
      CALL EXIT
      END
```

PAGE   2   **APPENDIX I PROGRAM 1: TAPE READING (Cont'd)**

```
VARIABLE ALLOCATIONS
   IMV(R )=0030-0008     D1(R )=0032          D2(R )=0034        NZER(I )=003A-0036      Q(I )=0045-003B   JREC(I )=0046
     I(I )=0047       IROW(I )=0048       IDAY(I )=0049          IHR(I )=004A       IMIN(I )=004B        JCOL(I )=004C
     J(I )=004D

STATEMENT ALLOCATIONS
 200  =0059  210  =005F  220  =0062  250  =0066  270  =006A  1    =00C3  10   =00D6  12   =00E2  15   =0101  20   =010F
 50   =0121  80   =0131  90   =013A  100  =015D

FEATURES SUPPORTED
 ONE WORD INTEGERS
 IOCS

CALLED SUBPROGRAMS
 SAVE    TRRED   FLD     FSTO    PRNTZ   PAPTZ   SRED    SWRT    SCOMP   SFIO    SIOAI   SIOFX   SIOF    SIOI    SUBSC
 SDFIO   SDWRT   SDCOM   SDAI    SDFX    SDI

INTEGER CONSTANTS
     1=0050    300=0051      0=0052    301=0053      4=0054     21=0055   7744=0056  24640=0057      3=0058

CORE REQUIREMENTS FOR ARG1
 COMMON      0  VARIABLES     80  PROGRAM    274

END OF COMPILATION

// DUP

*DELETE             ARG1
CART ID 0010   DB ADDR  343A   DB CNT   0017

*STORE      WS  UA  ARG1
CART ID 0010   DB ADDR  3B29   DB CNT   0017
```

PAGE 1 APPENDIX I PROGRAM 1A: PRINT-OUT

```
// JOB

LOG DRIVE   CART SPEC   CART AVAIL  PHY DRIVE
  0000        0010        0010        0000

V2 M10   ACTUAL 16K  CONFIG 16K

// FOR
*LIST ALL
*ONE WORD INTEGERS
*IOCS(DISK,1132PRINTER)
*NAME ARG1A
      REAL IMV(21)
      DIMENSION NARAY(20)
      DEFINE FILE 1 (300,45,U,JREC)
      DO 5 II=1,13
    5 NARAY(II)=II-1
      DO 40 M=1,3
      JREC=1
      WRITE(3,330)
      WRITE(3,320)
      WRITE(3,310)
      WRITE(3,270) (NARAY(II),II=1,13)
      WRITE(3,290)
      DO 30 I=1,300
      READ(1'JREC) IROW,IDAY,IHR,IMIN,JCOL,(IMV(J),J=1,JCOL)
      IF(IROW-999) 20,40,20
   20 L=IROW-1
      K=MOD(L,6)
      IF(K) 70,60,70
   60 WRITE(3,230)
      IF(JCOL-13) 70,70,66
   66 WRITE(3,240) IROW,IDAY,IHR,IMIN,(IMV(J),J=1,13)
      GOTO 30
   70 WRITE(3,240) IROW,IDAY,IHR,IMIN,(IMV(J),J=1,JCOL)
   30 CONTINUE
   40 CONTINUE
      JREC=1
      DO 45 I=1,300
      READ(1'JREC) IROW,IDAY,IHR,IMIN,JCOL,(IMV(J),J=1,JCOL)
      IF(JCOL-13) 440,440,75
   45 CONTINUE
      GOTO 440
   75 DO 76 II=14,20
   76 NARAY(II)=II-1
      DO 120 M=1,3
      JREC=1
      WRITE(3,330)
      WRITE(3,340)
      WRITE(3,350)
      WRITE(3,360) (NARAY(II),II=14,20)
      WRITE(3,370)
      DO 100 I=1,300
      READ(1'JREC) IROW,IDAY,IMIN,IHR,JCOL,(IMV(J),J=1,JCOL)
      IF(IROW-999) 80,100,80
   80 L=IROW-1
      K=MOD(L)
      IF(K) 90,85,90
   85 WRITE(3,320)
   90 WRITE(3,380) IROW,IDAY,IHR,IMIN,(IMV(J),J=14,JCOL)
  100 CONTINUE
  120 CONTINUE
  230 FORMAT(1X)
  240 FORMAT(1X,I3,2X,I3,2X,2I2,13(2X,F6.1))
  270 FORMAT(T7,'DAY',T13,'HR',13I8)
  280 FORMAT(T6,'----  ----',T18,13('  ----- '))
  310 FORMAT(T20,101('-'))
  320 FORMAT(T62,'CHANNEL  NUMBERS')
  330 FORMAT(1H1)
  340 FORMAT(T24,'CHANNEL  NUMBERS')
  350 FORMAT(T20,48('-'))
  360 FORMAT(T7,'DAY',T13,'HR',7I8)
  370 FORMAT(T6,'----  ----',T18,6('  -----  '))
  380 FORMAT(1X,I3,2X,I3,2X,2I2,6(2X,F6.1))
  440 CONTINUE
      CALL EXIT
      END
VARIABLE ALLOCATIONS
   IMV(R )=0030-0008 NARAY(I )=0045-0032  JREC(I )=0046        II(I )=0047         M(I )=0048          I(I )=0049
  IROW(I )=004A       IDAY(I )=004B        IHR(I )=004C       IMIN(I )=004D      JCOL(I )=004E          J(I )=004F
     L(I )=0050          K(I )=0051

STATEMENT ALLOCATIONS
 230  =005C  240  =005E  270  =006A  280  =0074  310  =0084  320  =008A  330  =0095  340  =0098  350  =00A3  360  =00A9
 370  =00B3  380  =00C4  5    =00ED  20   =015A  60   =016A  66   =0174  70   =0195  30   =01B4  40   =01BD  45   =01F6
 75   =0201  76   =0205  80   =0272  85   =0281  90   =0285  100  =02A4  1[illegible]0  =02AD  440  =02B6

FEATURES SUPPORTED
 ONE WORD INTEGERS
 IOCS

CALLED SUBPROGRAMS
 MOD      FLD      FSTO     PRNTZ    SWRT     SCOMP    SFIO     SIOFX    SIOIX    SIOI     SUBSC    SDFIO    SDRED    SDFX     SDI

INTEGER CONSTANTS
     1=0054      13=0055       3=0056    300=0057     999=0058       6=0059      14=005A      20=005B

CORE REQUIREMENTS FOR ARG1A
 COMMON       0  VARIABLES     84  PROGRAM    612

END OF COMPILATION

// DUP

*DELETE              ARG1A
CART ID 0010   DB ADDR  3411   DB CNT   0029

*STORE      WS  UA  ARG1A
CART ID 0010   DB ADDR  3B10   DB CNT   0029
```

PAGE 1 **APPENDIX I PROGRAM 2: SEMI-LOG CONVERSION (RAC)**

```
// JOB

LOG DRIVE   CART SPEC   CART AVAIL  PHY DRIVE
  0000        0010        0010        0000

V2 M10   ACTUAL 16K  CONFIG 16K

// FOR
*LIST ALL
*ONE WORD INTEGERS
*IOCS(CARD,1132 PRINTER)
*IOCS(DISK)
*NAME ARG2
      INTEGER CHANO(10)
      REAL IMV(10)
      DIMENSION JARAY(3),X(150,10)
      DIMENSION JROW(150),JD/ '(150),JHR(150),JMIN(150)
     2,TIME(150),Y(150,10),SL(10),Z(10),R(10),E(10),AA(10)
     3,YY(150,10),YYY(150),JJROW(150),TTIME(150)
      DEFINE FILE 1(300,45,U,JREC)
      EQUIVALENCE (IROWS,JARAY(1)),(IROWF,JARAY(2)),(NCHAN,JARAY(3))
      DATA X/1500*0.0/
      DATA Y/1500*0.0/
      DATA TIME/150*0.0/
      DATA YY/1500*0.0/
      DATA YYY/150*0.0/
      DATA JJROW/150*0/
      DATA TTIME/150*0.0/
      READ(2,300) IA
      DO 190  JJ=1,IA
      WRITE(3,225)
      CALL NOFI(3,JARAY,2)
      CALL NOFI(NCHAN,CHANO,2)
      WRITE(3,230) JARAY(1)
      WRITE(3,240) JARAY(2)
      WRITE(3,250) JARAY(3)
      WRITE(3,260) (CHANO(I),I=1,NCHAN)
      WRITE(3,270)
      JREC=IROWS
      NROW=IROWF-IROWS+1
      DO 50 M=1,NROW
      READ(1'JREC) IROW,IDAY,IHR,IMIN,JCOL,(IMV(J),J=1,JCOL)
      JROW(M)=IROW
      JDAY(M)=IDAY
      JHR(M)=IHR
      JMIN(M)=IMIN
      DO 10 K=1,NCHAN
      JCHAN=CHANO(K)+1
      X(M,K)=IMV(JCHAN)
   10 CONTINUE
   50 CONTINUE
      DO 60 M=1,NROW
      L=M-1
      K=MOD(L,6)
      IF(K) 55,52,55
   52 WRITE(3,280)
   55 WRITE(3,210) JROW(M),JDAY(M),JHR(M),JMIN(M),(X(M,K),K=1,NCHAN)
```

PAGE 2 **APPENDIX I PROGRAM 2: SEMI-LOG CONVERSION (RAC) (Cont'd)**

```
   60 CONTINUE
      WRITE(3,370)
      TTIME(1)=0
      DO 65 K=1,NCHAN
      YY(1,K)=ALOG(ABS(X(1,K)))
   65 CONTINUE
      JJROW(1)=JROW(1)
      IZ=1
      DO 130 M=2,NROW
      TIME(M)=(60*JHR(M)+JMIN(M))-(60*JHR(1)+JMIN(1))
      DO 120 K=1,NCHAN
      Y(M,K)=ALOG(ABS(X(M,K)))
  120 CONTINUE
      IF(TIME(M-1)-TIME(M)) 122,130,122
  122 IZ=IZ+1
      N=IZ
      JJROW(N)=JROW(M)
      TTIME(N)=TIME(M)
      DO 123 K=1,NCHAN
      YY(N,K)=Y(M,K)
  123 CONTINUE
  130 CONTINUE
      DO 150 N=1,IZ
      L=N-1
      K=MOD(L,6)
      IF(K) 140,135,140
  135 WRITE(3,340)
  140 WRITE(3,350) JJROW(N),TTIME(N),(YY(N,K),K=1,NCHAN)
  150 CONTINUE
      WRITE(3,370)
      DO 170 K=1,NCHAN
      DO 160 N=1,IZ
      YYY(N)=YY(N,K)
  160 CONTINUE
      CALL FITSL (IZ,TTIME,YYY,SLOPE,TINT,CORCO,SEE)
      SL(K)=SLOPE
      Z(K)=TINT
      R(K)=CORCO
      E(K)=SEE
      AA(K)=EXP(Z(K))
  170 CONTINUE
      DO 180 K=1,NCHAN
      WRITE(3,360) CHANO(K),SL(K),Z(K),R(K),E(K),AA(K)
  180 CONTINUE
  190 CONTINUE
  210 FORMAT(1X,I3,2X,I3,2X,2I2,10(2X,F6.1))
  225 FORMAT(1H1)
  230 FORMAT(1X,'INITIAL ROW NUMBER=',I3/)
  240 FORMAT(1X,'FINAL ROW NUMBER=',I3/)
  250 FORMAT(1X,'NUMBER OF CHANNELS='I2/////)
  260 FORMAT(1X,'CHANNEL  NUMBERS',3X,I2,9(6X,I2)//)
  270 FORMAT(T7,'DAY',T13,'HR')
  280 FORMAT(1X)
  300 FORMAT(1I3)
  340 FORMAT(1X)
  350 FORMAT(1X,I3,3X,F5.0,10(3X,F8.5))
  360 FORMAT(1X,I3,3X,F8.4,3X,F7.4,3X,F6.3,3X,F7.3,3X,F7.3)
```

PAGE   3 **APPENDIX I PROGRAM 2: SEMI-LOG CONVERSION (RAC) (Cont'd)**

```
  370 FORMAT(//////)
      CALL EXIT
      END
VARIABLE ALLOCATIONS
 IROWS(I )=0009        JARAY(I )=0009-0007 IROWF(I )=0008       NCHAN(I )=0007          X(R )=0BC0-000A  TIME(R )=0CEC-0BC2
     Y(R )=18A4-0CEE      SL(R )=18B8-18A6      Z(R )=18CC-18BA      R(R )=18E0-18CE      E(R )=18F4-18E2    AA(R )=1908-18F6
    YY(R )=24C0-190A     YYY(R )=25EC-24C2 TTIME(R )=2718-25EE    IMV(R )=272C-271A SLOPE(R )=272E       TINT(R )=2730
 CORCO(R )=2732          SEE(R )=2734        JROW(I )=27CD-2738  JDAY(I )=2863-27CE    JHR(I )=28F9-2864  JMIN(I )=298F-28FA
 JJROW(I )=2A25-2990 CHANO(I )=2A2F-2A26  JREC(I )=2A30          IA(I )=2A31           JJ(I )=2A32          I(I )=2A33
  NROW(I )=2A34            M(I )=2A35        IROW(I )=2A36        IDAY(I )=2A37         IHR(I )=2A38       IMIN(I )=2A39
  JCOL(I )=2A3A            J(I )=2A3B           K(I )=2A3C       JCHAN(I )=2A3D           L(I )=2A3E         IZ(I )=2A3F
     N(I )=2A40

STATEMENT ALLOCATIONS
 210  =2A4C  225  =2A58  230  =2A5B  240  =2A6A  250  =2A78  260  =2A8B  270  =2A9E  280  =2AA6  300  =2AA8  340  =2AAA
 350  =2AAC  360  =2AB5  370  =2AC2  10   =2B98  50   =2BA1  52   =2BBE  55   =2BC2  60   =2BE8  65   =2C1B  120  =2C7A
 122  =2C98  123  =2CDA  130  =2CE3  135  =2D00  140  =2D04  150  =2D2B  160  =2D52  170  =2D90  180  =2DB7  190  =2DC0

FEATURES SUPPORTED
 ONE WORD INTEGERS
 IOCS

CALLED SUBPROGRAMS
 NOFI     MOD      FALOG    FABS     FITSL    FEXP     FSUBX    FLD      FLDX     FSTO     FSTOX    FLOAT    CARDZ    PRNTZ    SRED
 SWRT     SCOMP    SFIO     SIOFX    SIOIX    SIOI     SUBSC    SDFIO    SDRED    SDFX     SDI

INTEGER CONSTANTS
     2=2A46       1=2A47       3=2A48       6=2A49       0=2A4A       60=2A4B

CORE REQUIREMENTS FOR ARG2
 COMMON       0  VARIABLES  10822  PROGRAM    900

END OF COMPILATION

// DUP

*DELETE             ARG2
CART ID 0010   DB ADDR  3B84   DB CNT   0275

*STORE       WS  UA  ARG2
CART ID 0010   DB ADDR  3BC4   DB CNT   0275
```

PAGE 1 APPENDIX I PROGRAM 3: MEAN AND STANDARD DEVIATION

```
// JOB

LOG DRIVE   CART SPEC   CART AVAIL  PHY DRIVE
  0000        0010        0010        0000

V2 M10   ACTUAL 16K  CONFIG 16K

// FOR
*LIST ALL
*ONE WORD INTEGERS
*IOCS(CARD,1132 PRINTER)
*IOCS(DISK)
*NAME ARG3
      INTEGER CHANO(10)
      REAL IMV(10)
      DIMENSION JARAY(3),X(150,10)
      DIMENSION JROW(150),JDAY(150),JHR(150),JMIN(150)
      DEFINE FILE 1(300,45,U,JREC)
      EQUIVALENCE (IROWS,JARAY(1)),(IROWF,JARAY(2)),(NCHAN,JARAY(3))
      READ(2,300) IA
      DO 150 JJ=1,IA
      WRITE(3,225)
      CALL NOFI(3,JARAY,2)
      CALL NOFI(NCHAN,CHANO,2)
      WRITE(3,230) JARAY(1)
      WRITE(3,240) JARAY(2)
      WRITE(3,250) JARAY(3)
      WRITE(3,260) (CHANO(I),I=1,NCHAN)
      WRITE(3,270)
      JREC=IROWS
      NROW=IROWF-IROWS+1
      DO 50 M=1,NROW
      READ(1'JREC) IROW,IDAY,IHR,IMIN,JCOL,(IMV(J),J=1,JCOL)
      JROW(M)=IROW
      JDAY(M)=IDAY
      JHR(M)=IHR
      JMIN(M)=IMIN
      DO 10 K=1,NCHAN
      JCHAN=CHANO(K)+1
      X(M,K)=IMV(JCHAN)
   10 CONTINUE
   50 CONTINUE
      DO 60 M=1,NROW
      L=M-1
      K=MOD(L,6)
      IF(K) 55,52,55
   52 WRITE(3,280)
   55 WRITE(3,210) JROW(M),JDAY(M),JHR(M),JMIN(M),(X(M,K),K=1,NCHAN)
   60 CONTINUE
      WRITE(3,310)
      WRITE(3,290)
      DO 110 K=1,NCHAN
      Z=0
      ZSQ=0
      TZ=0
      TZSQ=0
      SZSQ=0
```

PAGE 2 APPENDIX I PROGRAM 3: MEAN AND STANDARD DEVIATION (Cont'd)

```
      DO 100 M=1,NROW
      Z=X(M,K)
      ZSQ=Z**2
      TZ=TZ+Z
      TZSQ=TZ**2
      SZSQ=SZSQ+ZSQ
      IF(M-NROW) 100,70,100
   70 SD1=SZSQ/(M-1)
      SD2=TZSQ/(M*(M-1))
      SD=SQRT(SD1-SD2)
      SD=SD+SIGN(.05,SD)
      AVG=TZ/M
      AVG=AVG+SIGN(.05,AVG)
      DF=NROW-1
      WRITE(3,220) CHANO(K),AVG,SD,DF
  100 CONTINUE
  110 CONTINUE
  150 CONTINUE
  210 FORMAT(1X,I3,2X,I3,2X,2I2,10(2X,F6.1))
  220 FORMAT(2X,I3,2(11X,F6.1),11X,F3.0)
  225 FORMAT(1H1)
  230 FORMAT(1X,'INITIAL ROW NUMBER=',I3/)
  240 FORMAT(1X,'FINAL ROW NUMBER=',I3/)
  250 FORMAT(1X,'NUMBER OF CHANNELS='I2/////)
  260 FORMAT(1X,'CHANNEL  NUMBERS',3X,I2,9(6X,I2)//)
  270 FORMAT(T7,'DAY',T13,'HR')
  280 FORMAT(1X)
  290 FORMAT(1X,'CHANO',12X,'MEAN',12X,'STDEV',12X,'DF')
  300 FORMAT(1I3)
  310 FORMAT(//////)
      CALL EXIT
      END
```

PAGE 3 **APPENDIX I PROGRAM 3: MEAN AND STANDARD DEVIATION (Cont'd)**

```
VARIABLE ALLOCATIONS
 IROWS(I )=0009        JARAY(I )=0009-0007 IROWF(I )=0008       NCHAN(I )=0007            X(R )=0BC0-000A   IMV(R )=0BD4-0BC2
     Z(R )=0BD6          ZSQ(R )=0BD8          TZ(R )=0BDA       TZSQ(R )=0BDC         SZSQ(R )=0BDE      SD1(R )=0BE0
   SD2(R )=0BE2           SD(R )=0BE4         AVG(R )=0BE6         DF(R )=0BE8         JROW(I )=0C81-0BEC JDAY(I )=0D17-0C82
   JHR(I )=0DAD-0D18   JMIN(I )=0E43-0DAE CHANO(I )=0E4D-0E44  JREC(I )=0E4E           IA(I )=0E4F        JJ(I )=0E50
     I(I )=0E51        NROW(I )=0E52           M(I )=0E53       IROW(I )=0E54         IDAY(I )=0E55       IHR(I )=0E56
  IMIN(I )=0E57        JCOL(I )=0E58           J(I )=0E59          K(I )=0E5A        JCHAN(I )=0E5B         L(I )=0E5C

STATEMENT ALLOCATIONS
 210  =0E69  220  =0E75  225  =0E7E  230  =0E81  240  =0E90  250  =0E9E  260  =0EB1  270  =0EC4  280  =0ECC  290  =0ECE
 300  =0EED  310  =0FE2  10   =0FB8  50   =0FC1  52   =0FDE  55   =0FE2  60   =1008  70   =1063  100  =10B2  110  =10BB
 150  =10C4

FEATURES SUPPORTED
 ONE WORD INTEGERS
 IOCS

CALLED SUBPROGRAMS
 NOFI     MOD      FSQRT    FSIGN    FADD     FSUB     FLD      FLDX     FSTO     FSTOX    FDVR     FAXI     FLOAT    CARDZ    PRNTZ
 SRED     SWRT     SCOMP    SFIO     SIOFX    SIOIX    SIOF     SIOI     SUBSC    SDFIO    SDRED    SDFX     SDI

REAL CONSTANTS
  .500000E-01=0E62

INTEGER CONSTANTS
     2=0E64      1=0E65      3=0E66      6=0E67      0=0E68

CORE REQUIREMENTS FOR ARG3
 COMMON      0  VARIABLES   3682  PROGRAM    620

END OF COMPILATION

// DUP

*DELETE             ARG3
CART ID 0010   DB ADDR  3B09   DB CNT   002B

*STORE      WS  UA  ARG3
CART ID 0010   DB ADDR  3B09   DB CNT   002B
```

APPENDIX II REGRESSION ANALYSIS FOR PAIRED CURVE

```
                R           LogR      (LogR)^2       H2S         LogH2S    (LogH2S)^2
COL/ROW         1             2          3            4            5          6
   1          0.100        -1.000      1.000        0.010       -2.000      4.000
   2          0.300        -0.523      0.273        0.023       -1.638      2.684
   3          1.000         0.0        0.0          0.100       -1.000      1.000
   4          3.000         0.477      0.228        0.270       -0.569      0.323
   5         10.000         1.000      1.000        0.860       -0.066      0.004
   6         30.000         1.477      2.182        2.600        0.415      0.172
   7        100.000         2.000      4.000        9.000        0.954      0.911

CODE
?* 0

ANALYSIS
?* MU

NEW DATA
?* NO

SPECIFY THE DEPENDENT VARIABLE
?* 2

NO. INDEP VAR
?* 1

SPECIFY THESE VARIABLES
? 5

VARIABLE   REG.COEF.   STD.ERROR COEF.   COMPUTED T   BETA COEF.
    5       1.00530        0.01656        60.71373      0.99932

INTERCEPT                  1.05075
MULTIPLE CORRELATION       0.99932    (ADJUSTED R =    0.99932)
STD. ERROR OF ESTIMATE     0.04355    (ADJUSTED SE=    0.04355)

               ANALYSIS OF VARIANCE FOR THE REGRESSION
    SOURCE OF VARIATION          D.F.   SUM OF SQ.     MEAN SQ.    F VALUE
ATTRIBUTABLE TO REGRESSION        1        6.991         6.991    3686.157
DEVIATION FROM REGRESSION         5        0.009         0.002
    TOTAL                         6        7.001

PRINT RESIDUALS
?* YES

CASE NO   Y OBSERVED   Y ESTIMATED   RESIDUAL   STD.RESID.
   1        -1.000       -0.960       -0.040      -0.922
   2        -0.523       -0.596        0.073       1.684
   3         0.0          0.045       -0.045      -1.044
   4         0.477        0.479       -0.002      -0.045
   5         1.000        0.985        0.015       0.347
   6         1.477        1.468        0.009       0.211
   7         2.000        2.010       -0.010      -0.231

TEST OF EXTREME RESIDUALS
  RATIO OF RANGES FOR THE SMALLEST RESIDUAL.....      0.045
  RATIO OF RANGES FOR THE LARGEST RESIDUAL......      0.490
  CRITICAL VALUE OF THE RATIO AT ALPHA =.10 ...       0.434

SAVE ESTIMATES
?* NO
```

$\text{Log}\,R = 1.0053(\text{Log}\,H_2S) + 1.05076$

cc = .999+

Ratio for LARGEST RESIDUAL is higher than CRITICAL VALUE,
∴ one point Should Be DISCARDED.

APPENDIX II RE-ANALYSIS AFTER DISCARDING ONE POINT

```
               R          LogR     (LogR)^2       H2S   (LogH2S)^2  (LogH2S)^3
COL/ROW        1            2           3           4          5          6
   1         0.100       -1.000       1.000       0.010     -2.000      4.000
   2         1.000        0.0         0.0         0.100     -1.000      1.000
   3         3.000        0.477       0.228       0.270     -0.569      0.323
   4        10.000        1.000       1.000       0.860     -0.066      0.004
   5        30.000        1.477       2.182       2.600      0.415      0.172
   6       100.000        2.000       4.000       9.000      0.954      0.911

CODE
?* 0

ANALYSIS
?* MU

NEW DATA
?* NO

SPECIFY THE DEPENDENT VARIABLE
?* 2

NO. INDEP VAR
?* 1

SPECIFY THESE VARIABLES
? 5

VARIABLE    REG.COEF.   STD.ERROR COEF.   COMPUTED T   BETA COEF.
    5        1.02194        0.00860        118.80806     0.99986

INTERCEPT                   1.04481
MULTIPLE CORRELATION        0.99986   (ADJUSTED R =    0.99986)
STD. ERROR OF ESTIMATE      0.02027   (ADJUSTED SE=    0.02027)

              ANALYSIS OF VARIANCE FOR THE REGRESSION
   SOURCE OF VARIATION         D.F.   SUM OF SQ.     MEAN SQ.    F VALUE
ATTRIBUTABLE TO REGRESSION      1        5.802        5.802   14115.348
DEVIATION FROM REGRESSION       4        0.002        0.000
     TOTAL                      5        5.804

PRINT RESIDUALS
?* YES

CASE NO   Y OBSERVED   Y ESTIMATED   RESIDUAL   STD.RESID.
    1       -1.000        -0.999      -0.001      -0.046
    2        0.0           0.023      -0.023      -1.128
    3        0.477         0.464       0.013       0.662
    4        1.000         0.978       0.022       1.092
    5        1.477         1.469       0.008       0,406
    6        2.000         2.020      -0.020      -0.986

TEST OF EXTREME RESIDUALS
  RATIO OF RANGES FOR THE SMALLEST RESIDUAL.....      0.064
  RATIO OF RANGES FOR THE LARGEST RESIDUAL......      0.193
  CRITICAL VALUE OF THE RATIO AT ALPHA = .10 ...      0.482

SAVE ESTIMATES
?* NO
```

$\text{Log}\,R = 1.0219\,\text{Log}(H_2S) + 1.0448$

$CC = .999^{+}$

St. Error = .020 Modified
vs .044 Orig. Data